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October, 1940

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of the
AMERICAN CHEMICAL SOCIETY

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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To these charges of $2.50 and $5.00, respectively, per year, postage of $.20 per year must be added for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications for regular or for associate membership in the Division of Rubber Chemistry with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio, or to the Office of Publication, 1500 Greenmount Ave., Baltimore, Maryland.

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FALL MEETING OF THE DIVISION OF RUBBER CHEMISTRY, DETROIT, MICHIGAN, SEPTEMBER 12-13, 1940

The fall meeting of the Division of Rubber Chemistry was held in Detroit, September 12-13, during the one-hundredth meeting of the American Chemical Society. The technical sessions of the Division were held in the Commandery Asylum of the Masonic Temple, with an average attendance of four hundred and a peak attendance of about five hundred and fifty.

The first day was devoted primarily to a "Symposium on Rubber, Synthetics and Plastics in the Automotive Industry as Viewed by the Engineer and the Chemist", arranged by the Detroit Rubber Group, and comprising the following papers:

1. The Use of Rubber in the Automotive Industry from the Viewpoint of the Automotive Engineer.—C. Smart and G. W. Lampman.
2. The Use of Rubber in the Automotive Industry from the Viewpoint of the Rubber Technologist.—S. M. Cadwell.
3. The Standardization and Coördination of Automotive Rubber Parts Specifications.—L. A. Danse.
4. The Use of Synthetic Rubber in the Automotive Industry from the Viewpoint of the Automotive Engineer.—J. C. Zeder.
5. The Use of Synthetic Rubber in the Automotive Industry from the Viewpoint of the Rubber Technologist.—J. N. Street.
6. The Use of Plastics in the Automotive Industry.—W. M. Phillips.

Following the Symposium, Per K. Frolich of the Standard Oil Development Company of New Jersey presented a paper on a new synthetic rubber recently announced by his company. This paper, entitled "Butyl Rubber—A New Hydrocarbon Product", by R. M. Thomas, I. E. Lightbown, W. J. Sparks, P. K. Frolich, and E. V. Murphree, had been presented before the general meeting of the Society, and was kindly repeated for the benefit of the Division of Rubber Chemistry.

The first day's session closed with a report of the Crude Rubber Committee, presented by G. A. Sackett, Chairman.

At the two sessions held on September 13, the following papers were presented:

1. A Study of the Nitroparaffins and Their Derivatives as Heat Sensitizers for Compounded Rubber Latices.—Arthur William Campbell.

2. Creaming of Rubber Latex.—E. A. Hauser and B. Dewey, Jr.

3. Theoretical Stress-Strain and Compression Curves for Rubberlike Materials.—Eugene Guth and H. M. James.

4. The Crystallization of Vulcanized Rubber.—Norman Bekkedahl and Lawrence A. Wood.

5. Transparency of Rubber Compounds Containing Magnesium Carbonate. II.—W. F. Bixby and H. I. Cramer.

6. The Effect of Various Sulfur-Accelerator Ratios in Vulcanized Rubber as Shown by a Series of Laboratory Tests.—F. S. Conover.

7. Pliolite-Rubber Mixtures.—Herman R. Thies.

8. Vistanex Polybutene—Rubber Blends.—S. Longman.

9. Effect of Sulfur and Carbon Black Contents on Physical Properties of Perbunan Compounds.—C. A. Klebsattel.

10. Determination of Free Carbon in Rubber. The Cresol Method.—J. B. Roberts, Jr.

11. Test Formulas for Reclaimed Rubber.—Henry F. Palmer and Robert H. Crossley.

12. An Immersion Test for Rubber Compounds.—B. S. Garvey, Jr.

13. Effect of Petroleum Products on Neoprene Vulcanizates.—Donald F. Fraser.

14. A Torsional Hysteresis Test for Rubber.—M. Mooney and R. H. Gerke.

Six hundred and twenty-five members and guests attended the Divisional banquet held Thursday evening in the ballroom of the Book-Cadillac Hotel. M. A. Clark of the United States Rubber Company was toastmaster. During the dinner an excellent program of music and acrobatic acts was provided. The main speaker of the evening was W. J. Cameron of the Ford Motor Company.

The Division is indebted to the following companies for their generous contributions which made the entertainment possible.

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Wishnick-Tumpeer, Inc.
The Xylos Rubber Co.

The business meeting was held at the close of the last session. It was announced that the Goodyear Lecture Committee had received several nominations for the Goodyear Lecture for 1941, but that the Committee would not complete its deliberations until after the deadline for receiving nominations for 1941, *viz.*, November 15, 1940.

W. F. Busse submitted the written report of H. L. Trumbull, Chairman of the Nomenclature Committee. It was decided to publish the report in the next issue of RUBBER CHEMISTRY AND TECHNOLOGY.

C. R. Haynes, Chairman of the Membership Committee, reported a steady increase in membership to the point where the total number of members and associate members of the Division has passed the seven hundred point.

The Secretary, as Chairman of the Papers Committee, reported that a new set of rules governing the submission, approval and publication of papers presented before the Division had been approved by the Executive Committee at its meeting the previous day. The report of the Committee was accepted, and the new rules as approved by the Executive Committee were adopted. (These new papers rules appear elsewhere in this issue.)

The Chairman reviewed in detail the revision of the By-Laws of the Division relating to elections, as recommended by a committee headed by W. F. Busse and approved by the Executive Committee. This report was accepted and the revised By-Laws therein recommended were adopted. The revisions are as follows:

Section 6 is cancelled and replaced by the following:

ELECTIONS. All elections shall be by secret ballot.

The Nominating Committee shall submit a report at the Spring Meeting, following which report the Chairman shall invite nominations from the floor.

A printed ballot, carrying the names of the nominees arranged in alphabetical order, for each office shall be mailed to each Member by the Secretary, at least thirty days before the Annual Meeting. The ballots shall be opened and counted at the time of the Annual Meeting of the Society by a Tellers Committee appointed by the Chairman.

The Chairman shall not be eligible for reëlection for the ensuing year. Three of the five Directors shall be elected by The Division for a term of one year, starting at the close of the Annual Meeting at which the election is held. The outgoing Chairman and the nominee for Vice-Chairman receiving next to the largest number of votes for that office shall be directors for the ensuing year. No Director shall be eligible for re-election as a Director for the ensuing year. Each Member shall vote for not more than three (3) nominees for Director. The three nominees for Director receiving the largest number of votes shall be declared elected. In the event of an indecisive vote because of a tie, those nominees receiving the same number of votes shall be voted on by the Members present at the Annual Meeting until the tie is removed. In the event that there is no Annual Meeting, the tie shall be removed by the vote of the outgoing Executive Committee. Officers shall take office at the close of the Meeting at which they are elected, and shall serve for one year, or until their successors are elected.

Section 9, MEETING, second paragraph, is changed to read:

Fifty (50) Members shall constitute a quorum for any Business Meeting of The Division.

SECTION 10, APPOINTED COMMITTEES, (A) Nominating Committee, is changed to read:

A Nominating Committee of five (5) Members shall be appointed not later than March 1 of each year. This Committee shall select at least one (1) nominee for each office to be voted on at the Annual Meeting and at least two (2) nominees for Vice-Chairman.

The report of the Nominating Committee was submitted by L. B. Sebrell, Chairman. As a result of the ballot then taken the following officers were elected for 1940-41:

Chairman	R. H. Gerke.
Vice-Chairman	J. N. Street.
Secretary	H. I. Cramer.
Treasurer	C. W. Christensen.
Sergeant-at-Arms	C. P. Hall.
Directors	E. B. Curtis.
	Walter Juve.
	O. M. Hayden.
	Bruce R. Silver.
	F. S. Malm.

R. H. Gerke, Chairman of the Planning Committee, reported that this committee was considering a number of possible symposia to be held at the coming meeting in St. Louis. He urged all members to submit to this committee for consideration their suggestions for subjects suitable for symposia.

It was duly voted that the Secretary be instructed to transmit to the officers of the Detroit Rubber Group the following resolution:

Be It Resolved, That the Secretary convey to the officers and members of the Detroit Rubber Group the appreciation of the Division of Rubber Chemistry of the excellent work of the Group in arranging the special "Symposium on Rubber, Synthetics and Plastics in the Automotive Industry," and in handling all local arrangements for the meeting and the banquet, all of which contributed to the outstanding success of this meeting.

Secretary's Report:

Total Membership to date, August 31, 1940		699
Members paid for 1940	549	
Associate Members paid for 1940	150	
New Members and Associate Members from March 31, 1940 to August 31, 1940 (included in above figure)		55
Regular Members	30	
Associate Members	25	
Subscriptions to *Rubber Chemistry and Technology*		347
Honorary Members and Exchanges		24

H. I. CRAMER, *Secretary.*

NEW PAPERS RULES

ADOPTED BY THE EXECUTIVE COMMITTEE OF THE DIVISION OF RUBBER CHEMISTRY AT DETROIT, SEPTEMBER 13, 1940

I. SUBMISSION. Each author intending to present a paper before the Division of Rubber Chemistry shall submit to the Secretary, by the usual deadline set by the Society (approximately 8 weeks before the beginning of each semi-annual convention), the title of his paper, three copies of an abstract of 200 to 250 words, an estimate of the time which will be needed for presentation, and the name of the laboratory in which the work was done.

II. APPROVAL. Each paper shall be approved by a Papers Committee, consisting of the Editor of RUBBER CHEMISTRY AND TECHNOLOGY, the Secretary, and a Member of the Division appointed by the Chairman, before it is placed on the final program.

III. PUBLICATION.

1. Three copies of the complete manuscripts of all papers accepted for presentation before the Division shall be submitted to the Secretary on, or prior to, the date of presentation.

2. The author of the paper shall designate the journal to which the manuscript shall be submitted. Publication of the paper shall follow one of four procedures:

a. Original publication, when the paper is of interest and value to non-rubber chemists, in one of three Society journals: *Industrial and Engineering Chemistry, Journal of the American Chemical Society* or *Journal of Physical Chemistry,* depending on the purport and contents of the paper.

b. Original publication as in case (a), with subsequent publication, by release of copyright, in RUBBER CHEMISTRY AND TECHNOLOGY.

c. Original publication in RUBBER CHEMISTRY AND TECHNOLOGY when the paper is of interest and value chiefly to rubber chemists, and this is agreed to by the editor of the Society journal in which the paper might otherwise be published.

d. Direct release, subject to rules of the American Chemical Society, to an independent publication not under the editorial supervision of the Society.

3. The Secretary of the Division shall furnish the editor of the journal which has been chosen for publication with two copies of all manuscripts submitted. At the same time he shall transmit to the editor the names of two men, selected by the Papers Committee, to whom each manuscript may be sent for review prior to publication.

REPORT OF THE COMMITTEE ON NOMENCLATURE

DIVISION OF RUBBER CHEMISTRY, AMERICAN CHEMICAL SOCIETY

Progress in both the science and technology of elastic materials has been so rapid that our knowledge of them has outstripped efforts to provide an adequate vocabulary. Many will agree to the need for a revision and extension of the nomenclature. Fewer may agree to the exact nature of proposed changes. There is a need for more precise definitions of terms, as well as the invention of new terms. The Committee seeks the coöperation of those who are interested, and to this end offers a number of suggestions, and makes certain proposals.

The needs with respect to words have been well reviewed by Dawson[1] in a paper "On Rubber Terminology". This paper indicates by numerous examples the types of confusion that exist. It does not, however, make specific recommendations for means of clarification.

An important section of the work on terminology is that which relates to synthetic materials which are rubberlike in character. Fisher[2] has made a valuable contribution with respect to the terminology of these materials in a paper on the "Nomenclature of Synthetic Rubbers". Since his paper is a rational attempt to accept, invent, and define terms it may serve as a guide for the present, even though there may be reasonable disagreement with some of the selections made, and amendments will be necessary from time to time.

The term *rubber* itself has been used to designate so many things as to make it entirely lacking in specificity. The varied meanings associated with the word rubber have become so well established that it would probably be fruitless, if not needless, to attempt a reduction in their number.

In the case of the term, *synthetic rubber,* it would be well to avoid such a multiplicity of meanings. No good purpose would be served, however, by trying to limit its use to designate a synthetic material identical with natural rubber, since the latter is such a variable substance. Because the chemistry of these polymeric substances is somewhat obscure, and the only chemical property common to all of them is that of high molecular weight, a definition of synthetic rubber can best be made to depend on the physical properties of the product.

Of a number of attempts to define this term, perhaps the best is that of Midgley[8]. He says: "synthetic rubbers are those organic substances which possess the property of forcibly retracting to approximately their original size and shape after being greatly distorted, *i.e.*, such as being stretched x per cent of their original lengths. Here x is some arbitrary value. It should be over 100, probably 400, possibly 600, but certainly not higher". It may be suggested, however, that the term, "synthetic rubber", should be restricted to the polymers obtained from monomeric organic substances containing conjugated double or triple bonds, or co-polymers involving these materials.

In the search for names for the ever-increasing list of polymeric substances, it is well to attempt their classification, and this can satisfactorily be based on their chemical composition. The following classification is offered by way of example:

SYNTHETIC POLYMERIC SUBSTANCES

I. Inorganic.
II. Organic.
  A. Saturated polymers with only carbon atoms in the chain.
    a. Hydrocarbons.
    b. Substituted hydrocarbons.
      1. Containing halogen (made from vinyl halide).
      2. Containing acid, ester, or nitrile groups.
      3. Co-polymers of (1) and (2).
  B. Unsaturated polymers with only carbon atoms in the chain.
    a. Hydrocarbons (polymers of butadiene and its homologs, and of monomers containing more than one point of unsaturation).
    b. Co-polymers involving butadiene and its homologs.
    c. Halogen-containing polymers of butadiene and homologs.
    d. Alkoxy or aryloxy containing polymers of butadiene and its homologs.
    e. Acid, ester, or nitrile derivatives of butadiene and its homologs.
    f. Thioplastics.
  C. Polymers in which oxygen, nitrogen, and perhaps sulfur, as well as carbon, enter into the formation of the chain.
    a. Polymeric amides.
    b. Polymeric esters.
      1. Aliphatic acid esters.
      2. Alkyd resins.
  D. Derivatives of cellulose.
  E. Derivatives of urea.
  F. Reaction products of phenolic substances with aldehydes.
  G. Derivatives of natural rubber.
    a. Thermoprenes.
    b. Reaction products obtained by the action of stannic chloride, aluminum chloride, etc.
    c. Reaction products with halogen acids.
    d. Reaction products with halogens.

Of course not all these materials are rubberlike, and many are not of direct concern to the rubber technologist. Nevertheless, it is well to recognize their existence to avoid including inappropriate examples in the definitions of terms.

In some cases the rubberlike properties of elasticity and plasticity are engendered in the materials; in other cases they are merely enhanced by the incorporation of high boiling liquids called "plasticizers". These have also been referred to as "elasticizers", "elasticators", or even "softeners".

Natural rubber has two outstanding characteristics, unusual elasticity and vulcanizability. Synthetic rubberlike polymers possess these characteristics in varying degrees, and the former characteristic has been made a part of the definition of synthetic rubber. The latter should be used as a basis for classification or differentiation.

Thus arises the necessity of defining *vulcanization*. Thus far in the literature vulcanization has been defined with reference to natural rubber, although it is

now used in connection with synthetic rubber. It has been used to identify the process of forming both soft rubber vulcanizates and ebonite. This is unfortunate, and while usage sanctions this multiple service of the term with respect to natural rubber, it would be well to confine the term vulcanization, with respect to synthetic polymers, to the process which forms products with an elasticity akin to that of soft rubber vulcanizates, and to select a new term to refer to the formation of hard polymers resembling ebonite. Such a word might be *ebonation* (verb: *ebonize;* noun: *ebonizate* or *ebonate*).

Definitions of vulcanization have formerly emphasized the chemical process involved, *e.g.*, Babcock[4] says: "Vulcanization as ordinarily conceived can be defined as the process of combining sulfur with rubber under the influence of heat." He notes, however, that the recent definitions stress not the chemistry involved, but the physical changes which take place. Kindscher[5] says: "The process of vulcanization then transforms the rubber from the plastic into the elastic condition so essential for practical use."

Dawson and Porritt[6] say: "Vulcanization is any process which converts raw rubber into a product insoluble in most solvents, less sensitive to temperature changes, and of increased elastic and less plastic properties."

Williams[7] says: "Vulcanization is essentially a process which reduces the plastic properties of the rubber, and is accompanied by an increased resistance to solvents and an increased resistance to hardening at low temperatures." In another place[8] he says: "In the broadest sense vulcanization to produce soft vulcanized rubber is any treatment which maintains the elasticity of the rubber while its plasticity is decreased."

What then is to be the definition of vulcanization as it refers to synthetic materials? On questioning a number of specialists in the field of synthetic polymers, there was found to be a unanimity of opinion that plasticized polyvinyl chloride, Thiokol, and polyisobutylene are not vulcanizable, although at least the first two can be made to undergo some partial decrease in thermoplasticity by a heat treatment in the presence of proper catalysts. If the definition of vulcanization excludes these changes or, worse, does not make any disposition of them, then an author will resort to the very unfortunate expression "socalled vulcanization". It will probably be necessary, therefore, to have a word or words to represent more accurately this apologetic expression.

It would be helpful to an understanding of the literature if every author carefully indicated whether he was referring to the unvulcanized or the vulcanized forms of polymers under consideration. This could be done very simply by using the accepted name of the polymer for the unvulcanized form, and prefacing the name with v. for the vulcanized form.

It should be emphasized that all monomers should have different names from their corresponding polymers. This is in general the case, for, where only one monomer is involved in the polymerization, the polymer has the same name prefaced by *poly*, *e.g.*, isoprene, chloroprene, bromoprene, phenoprene, alkoxyprene. The polymer may also be given a distinctive trade name, *e.g.*, Neoprene. Those polymers above, having the *prene* ending, are included in the generic term *polyprenes*. The *prene* ending has been used to designate the analogs of isoprene, and the materials indicated are monomers unless the word is prefaced by *poly*, except for the term thermoprenes. The latter refers to a quite different variety of materials, presumably cyclicized derivatives of natural rubber, and is so well established through long usage that it must be accepted.

With respect to other generic terms, there is no need for the multiplicity of words, such as thioplastics, thioplasts, and thiomers. The first one should be sufficient, and sufficiently characteristic, unless one should prefer to emphasize the most outstanding characteristic of these materials and call them thiodors.

Just as the adjective, synthetic, has now become also a noun, so has the adjective, elastic, become a noun, and we have a generic class called *elastics*. So have we also a class of *plastics*. There seems no need, however, for the elided word lastics, or the extended word elastoplasts.

We have had for some time the words *monomer* and *polymer*. Now we have the words *co-monomer* and *co-polymer*. The meaning of the latter is easily evident, but one may wish to know what meaning can be ascribed to the former. The two words do not have parallel meanings, co-monomer referring to that unit entering into the formation of the co-polymer which is added to vary the properties of the polymer obtained in its absence; acrylic nitrile, for example, is the co-monomer when added to butadiene.

Although many hyphenated words lose their hyphens in the course of time, it would be well to retain the hyphens in co-monomer and co-polymer until the words have become more familiar through longer use. The hyphen certainly aids laymen to correct pronunciation.

We have the words *plasticize, plasticizer,* and *plasticization*. Why not also *plasticate, plasticator,* and *plastication?* One hears these latter terms, *e.g.*, "Gordon plasticator", but looks for them in vain in dictionaries and in glossaries of technical terms. They perhaps are an unnecessary duplication, except that plastication is easier to say than plasticization. What then of *plastify*, rhyming with mystify, and *plastifier,* and plastification?

How does plasticization differ in meaning from mastication? It would perhaps be well to limit the term *mastication* to the process of working rubber or synthetic rubbers on open mills or calenders, and plasticization to the process involving essentially heat (with or without mixing) or a combination of heat and a chemical activator for the softening process. A plasticator, as mentioned above, can be the name of a machine for plasticizing rubber, but it would be confusing to name the chemical aid to plasticization a plasticizing agent, for the latter expression has been used to represent softeners added to rubber or synthetic rubber to increase the plasticity or vinyl compounds to change horny modifications, by a swelling action, into gels that are more or less rubberlike. The chemical aids to plasticization have been called "mastication accelerators".

There are other problems of nomenclature which need clarification, and these should be considered by the Committee at a later time. The present report summarizes the more pressing problems, suggests some remedies to avoid confusion, and indicates the need for both elaboration and simplification of terminology which, it is hoped, may encourage others to express themselves in ways that will be philologically useful.

REFERENCES

[1] Dawson, *Proc. Rubber Tech. Conf. London,* **1938**, p. 1003; RUBBER CHEM. TECH. **12**, 411 (1939).
[2] Fisher, *Ind. Eng. Chem.* **31**, 941 (1939); RUBBER CHEM. TECH. **12**, 900 (1939).
[3] Midgley, "The Chemistry and Technology of Rubber", Edited by Davis and Blake, New York, **1937**, p. 679.
[4] Babcock, *Ind. Eng. Chem.* **31**, 1198 (1939).
[5] Kindscher, "The Science of Rubber", Edited by Dunbrook and Morris (Am. Ed. of Memmler), New York, **1934**, p. 270.
[6] Dawson and Porritt, "Rubber—Physical and Chemical Properties", Res. Assoc. Brit. Rubber Manufrs., Croydon, **1935**, p. 603.
[7] Williams, "Polymerization", Edited by Burk, Thompson, Weith and Williams, New York, **1937**, 167.
[8] Williams, "The Chemistry and Technology of Rubber", Edited by Davis and Blake, New York, **1937**, p. 237.

H. L. TRUMBULL, *Chairman*
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AMERICAN SOCIETY OF MECHANICAL ENGINEERS

SUBDIVISION ON RUBBER AND PLASTICS

A series of meetings will be sponsored by the Subdivision on Rubber and Plastics at the annual meeting of the A.S.M.E. to be held at the Hotel Astor, during the week of December 2.

The papers to be presented at the Rubber and Plastics meetings, as well as the dates and times, are:

Session 1

December 5—9: 30 a. m.

1. Design and Application of Phenolic Resin Asbestos Compositions in Corrosion Resistant Equipment, W. H. Adams, Haveg Corp., Newark, Del.
2. Rubber Springs—Compression Loading, J. F. Downie Smith, Research Division, United Shoe Machinery Corp., Beverly, Mass.

Session 2

December 5—2: 00 p. m.

1. The Creep of Natural and Synthetic Rubber Compounds in Shear, Ivan Gazdik and S. H. Hahn, B. F. Goodrich Co., Akron, O.
2. Notes on the Creep of Neoprene in Shear, F. L. Yerzley, Rubber Chemicals Division, E. I. du Pont de Nemours & Co., Wilmington, Del.

Technical representatives of companies engaged in either the production or use of rubber and plastics are invited to attend these meetings.

NEW BOOKS AND OTHER PUBLICATIONS

RUBBER: HISTORY, PRODUCTION AND MANUFACTURE. P. W. Barker. Published by Bureau of Foreign & Domestic Commerce. 6 x 9 in. 48 pp. Available from Superintendent of Documents, Washington, D. C., at 10c a copy.

Each year the Leather & Rubber Division of the Bureau of Foreign & Domestic Commerce receives hundreds of requests for information of a general character pertaining to rubber. These inquiries are received from rubber manufacturers, importers and dealers, from brokerage and investment houses, from college and graduate students, and from the general public. It is with these inquiries in mind that the current booklet was prepared. Two earlier editions of a general circular on rubber have been completely exhausted. The new booklet is devoted largely to the subject of the production of rubber rather than to manufacture of rubber products. After a brief history of the industry is given, various plantation methods are discussed. Some space is also devoted to a discussion of restriction. Several statistical tables are included. [From *The Rubber Age* of New York.]

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY—1939. (Vol. 3). Edited by T. J. Drakeley. Published by the Institution of the Rubber Industry, 12, Whitehall, London, S.W.1, England. 7¼ x 9½ in. 164 pp. Price to members: 2/6 (approximately 60c); to nonmembers: 10/6 (approximately $2.60).

Third in the annual reports issued by the I.R.I. to keep its members and the industry in general abreast of latest developments in all branches of the industry, from cultivation through to manufacture of finished products, this edition covers the year 1939. As in the previous issues, coverage of each group of developments is entrusted to an outstanding authority. Complete bibliographical references permit the reader to secure further data on any particular subject, while subject and author indexes make his task still easier. The various chapters and their authors follow:

Historical and Statistical Review, C. J. Redfern and W. F. V. Cox; *Planting and Production of Raw Rubber, Latex, Gutta-Percha, Balata, Chicle and Jelu-*

tong, J. Grantham; *Properties, Applications and Utilization of Latex, Including Treatment of Fabric with Latex,* C. F. Flint; *Chemistry and Physics of Raw Rubber and Rubber Derivatives, Gutta-Percha, Chicle, Balata and Jelutong,* W. J. S. Naunton; *Synthetic Rubber,* Maldwyn Jones; *Testing Equipment and Specifications Other Than for Latex,* W. J. S. Naunton; *Compounding Ingredients, Accelerators, Antioxidants and Softeners,* F. H. Cotton; *Fibres and Textiles,* F. Chadwick; *Chemical and Physical Properties of Vulcanized Rubber,* A. E. T. Neale; *Tires,* J. G. MacKay; *Belting,* G. F. Payne; *Hose and Tubing,* J. Kirkwood; *Cables and Electrical Insulation,* H. A. Daynes; *Footwear,* R. C. Davies; *Games, Sport Accessories and Toys,* J. P. Griffiths; *Mechanical Rubber Goods,* Herbert Rogers; *Roads,* G. E. Coombs; *Flooring,* J. Kirkwood; *Surgical Goods,* C. R. Pinnell; *Textile-Rubber Composites, Solvents and Cements,* W. N. Lister; *Sponge Rubber,* J. D. Campbell; *Hard Rubber,* B. L. Davies; *Works Processes and Materials,* B. L. Davies; and *Machinery and Appliances,* E. Morris. [From *The Rubber Age* of New York.]

DEFENSE OF THE UNITED STATES AND OTHER NATIONS IN THE WESTERN HEMISPHERE: RUBBER. 6 x 9 in. 32 pp. Available from Superintendent of Documents, Washington, D. C., for 10c a copy.

This is a printed record of the testimony given by John L. Collyer, President, B. F. Goodrich Co.; W. S. Farrish and Frank A. Howard, representing the Standard Oil Co. of New Jersey, and E. R. Bridgwater, Manager, Rubber Chemicals Department, E. I. du Pont de Nemours & Co., Inc., presented to the Committee on Military Affairs of the U. S. Senate on June 14, 1940, on S. 4082, a bill to provide for the defense of the people of the United States and other nations in the Western Hemisphere as may desire the coöperation and assistance of this country. The testimony given comprises an interesting report on the current status of synthetic rubber manufacture in the United States, as well as its possibilities in the event of any emergencies. Like all records of hearings, it is printed in question-and-answer form. [From *The Rubber Age* of New York.]

WHERE TO FIND THE NEW TRADE NAMES. Compiled and published by Alice M. Amoss, Librarian, Technical Library, Edgewood Arsenal, Maryland. 6 x 9 in. 32 pp. 75c.

This is a bibliography giving sources of reference books, directories, journals, etc., containing brand and trade names of products and materials of all descriptions. It is intended for use by research technologists and purchasing agents who may be interested in locating the source of supply of some particular branded product, its properties or its uses. The various directories are listed under miscellaneous classifications, ranging from abrasives to wire. Rubber and Rubber Chemicals and Rubberized Coatings are two of the many classifications. [From *The Rubber Age* of New York.]

RUBBER AS AN ENGINEERING MATERIAL. Published by the B. F. Goodrich Co., Akron, Ohio. 8½ x 11 in. 25 pp. 50c per copy.

Data on rubber as a material—its various forms, properties and limitations—are presented in concise fashion in this handbook. The material was prepared for use by the practical worker, with formulas, tables and graphs carefully avoided. Ten chapters in all are included, these being: Forms of Manufactured Rubber; Properties; Resistance to Corrosion; Resistance to Abrasion, Cutting, Tearing and Impact; Elasticity; Vibration, Shock and Noise Isolation; Heat Resistance and Insulation; Resistance to Oils and Solvents; Properties of Elastic Syn-

thetics; and Testing of Rubber Products. Profusely illustrated, this handbook should prove of special value to mechanical and other engineers. [From *The Rubber Age* of New York.]

RUBBER PRODUCING COMPANIES—1940. Compiled by the Mincing Lane Tea & Rubber Share Brokers' Association, Ltd. Published by The Financial Times, Ltd., 72 Coleman St., London, E. C. 2, England. 5¼ x 8 in. 614 pp. 8s/1½d (approximately $2.00).

The latest revised edition of this "Official Guide for Investors in Rubber Shares", contains details on approximately 550 separate undertakings. Data given include forward sales, capitalization per planted acre, investments and reserves. A valuable feature is the analysis of results of each estate for the past few years, many of them extending to the end of 1939. These analyses show estate areas, standard outputs, annual production, gross price, "all-in" cost, net profit, dividends, and carry-forwards. Directors, officers and secretaries of each plantation operator are given wherever possible. Although primarily devoted to companies engaged in rubber cultivation, concerns with interests in tea, coffee, coconuts and palm oil, supplementary to their interest in rubber, are also listed. [From *The Rubber Age* of New York.]

RUBBER LATEX COMPOUNDING. (Report No. 40-1). Benton Dales and William H. Ayscue. Rubber Chemicals Division, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware. 6¼ x 9¼ in. 56 pp.

Through the brief discussion of the history and general properties of latex, effects of compounding ingredients, and outstanding latex applications, this laboratory report provides an excellent working background of pertinent information for the user or prospective user of latex. The sources, composition, preparation and general compounding of latex are dealt with, as are the preparation of compounding ingredients, latex compositions and test films. One section is devoted to accelerators, protective chemicals, stabilizers, thickeners and other compounding ingredients. Another section, one of the most complete in the report, deals with the various processes used in the manufacture of latex products, including dipping, molding, electrodeposition and impregnating and coating. Formulas for the production of toy balloons, gloves, thread, adhesives, and other articles are given. A complete subject index is a valuable part of the report. [From *The Rubber Age* of New York.]

ANNUAL SURVEY OF AMERICAN RUBBER CHEMISTRY FOR 1937. Webster N. Jones, Published as Engineering Bulletin 86 of the Carnegie Institute of Technology, Pittsburgh, Pa. 64 pages. Price 75c.

The previous edition of this review, which covered the year 1936, appeared in 1937. The publication this year of the survey for 1937, although late, will be welcomed by all those following the advances in rubber chemistry and technology. The present survey is based on 326 American patent and periodical references, with the subject matter divided into the following classifications: crude rubber, properties and structure of rubber, accelerators, retarders of vulcanization, plasticizers, age-resisters, compounding ingredients and compounding, control and testing, reclaiming latex and rubber dispersions, cements and adhesives, rubber technology, synthetic rubber and rubberlike products, derivatives of rubber, and miscellaneous. The continuation of this annual survey should

be urged, particularly as it may be used to serve as a supplement to the Division of Rubber Chemistry's A. C. S. monograph, "Chemistry and Technology of Rubber", which appeared in 1937 under the editorship of C. C. Davis and J. T. Blake. [From the *India Rubber World.*]

PRACTICAL LATEX WORK. H. J. Stern. The Blackfriars Press, Ltd., Leicester, England. 1940. 4½ by 7¼ inches, 103 pages. Illustrated. *India Rubber World,* U. S. agent. $1.50 postpaid.

In 1938 and 1939 there appeared in *The Rubber Age* of London a series of articles by H. J. Stern on latex work. They aroused so much interest that Dr. Stern revised them and published them in the form of this small book.

The first three chapters are devoted to discussions of the types of latex available, methods and equipment used in preparing dispersions and incorporating them into latex, and properties of ingredients commonly used in latex compounds. The next three chapters discuss manufacturing operations and equipment, including dipping, spreading, and the preparation and use of vulcanized latex. The final chapter describes methods of costing in latex manufacture.

This book gives excellent, brief discussions of methods and equipment used in many present-day industrial applications of latex. It contains a surprising amount of useful detailed information for a work of its length. [E. G. Partridge.]

MANUAL DE LA INDUSTRIA DE LA GOMA. Luis Pascual Majias Lopez. Published by *La Goma,* Calle de Moncada, 4, Tda., Barcelona, Spain. 6½ x 9½ in. 362 pp. $3.00. (In Spanish only.)

When this book was reviewed in the April, 1940, issue of this journal we stated that it was a condensed version in Spanish of the "Encyclopedie du Caoutchouc et des Industries qui s'y Rattachent", the French manual issued several years ago by the *Revue Generale du Caoutchouc.* We arrived at this conclusion because some of the identical illustrations were used and many of the chapter heads were the same. It now develops, however, that although the publishers of the Spanish manual purchased a number of the engravings from the publishers of the French manual, and despite the similarity of chapter heads, the Spanish manual is a completely original work prepared by Senor Lopez. We are glad to bring this version to the attention of our readers.

The *Manual de la Industria de la Goma* consists of 49 chapters, 37 devoted to rubber and the balance to applications of latex. In addition, there is a section giving a number of tables of interest to compounders of rubber products, including data on vulcanization temperatures, types of crude rubber and commercial solvents. The entire range of rubber, from collection through to the manufacture of the finished product, is covered in the manual. After discussing methods of cultivation, theories of vulcanization, vulcanization processes, compounding ingredients, use of factice, and recovery of solvents, the author launches into a number of chapters each devoted to the manufacture of some other rubber product, including tires and tubes, wires and cables, footwear, thread, and hard rubber goods.

Although formulas are given throughout the book in connection with the manufacture of specific products, there is in addition a complete chapter devoted to general formulas. In many cases alternative formulas are given, so that the user of the manual may do his own experimenting to determine which of the formulas given is best suited for his purpose. Incidentally, the manual is the first comprehensive work on rubber which has yet appeared in the Spanish language. [From *The Rubber Age* of New York.]

THE PARTICLE SIZE AND SHAPE OF COLLOIDAL CARBON AS REVEALED BY THE ELECTRON MICROSCOPE. Columbian Carbon Co., 41 East 42nd St., New York City. 5½ x 7¾ in. 56 pp.

Issued as Vol. II of "Columbian Colloidal Carbons", this booklet presents a review of all previous work designed to determine the particle size and shape of colloidal carbon and so master the mystery of colloidal carbon-rubber reinforcement, describes the various forms of electron microscopes which have been constructed in recent years, and then gives the results of the first of a series of investigations being conducted by W. L. Wiegand and his associates with the electron microscope as applied to Micronex carbon black. The conclusions drawn from this initial investigation indicate that all previous theories on the particle diameter of carbon black may have to be considerably revised. [From *The Rubber Age* of New York.]

THE CARE AND TREATMENT OF RUBBER FLOORING. British Rubber Publicity Association, 1, Albert Mansions, Lansdowne Road, Croydon, Surrey, England, 5½ x 8½ in.

Proper methods of washing and polishing rubber floors are given in this booklet. The point is stressed that only a cleanser or polish recommended by the manufacturer of the flooring should be used, and that all "home remedies" should be discarded or given thorough tests before application. [From *The Rubber Age* of New York.]

TEXTILE TESTING. John H. Skinkle. Published by Chemical Publishing Co., Inc., 148 Lafayette St., New York City. 5½ x 8 in. 272 pp. $3.00.

Methods for the physical, chemical and microscopical testing of textiles are thoroughly discussed in this book which is divided into three parts, each devoted to one of the three phases of examination. Where several methods are available, the author, who is an assistant professor of textile chemistry at Lowell Textile Institute, gives that considered best in detail and makes brief mention of the others. At the end of the description of each test a bibliography of references is given, so that those desiring further information can secure it. Brief reference is made to a rubber extraction device recommended by the A.S.T.M. for determining oil and grease in knit goods with carbon tetrachloride. The book has 17 chapters, 27 tables, and numerous illustrations, graphs and sketches. [From *The Rubber Age* of New York.]

HEVEA LATEX: EFFECT OF PROTEINS AND ELECTROLYTES ON COLLOIDAL BEHAVIOR *

A. R. KEMP and W. G. STRAITIFF

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It is generally recognized that the protein adsorbed on the rubber particles in *Hevea* latex plays a predominant rôle in connection with stability and coagulation phenomena. Although the function of proteins as protective substances in colloidal dispersions is well known, very little exact information is available regarding the mechanism of their protective action.

Different latices containing protein have been found to differ markedly in colloidal stability. For example, *Hevea* latex is coagulated by the addition of protein coagulants, whereas *Balata* (*Mimusops globosa*) and *Funtumia elastica* latices also contain protein but are not coagulated by the addition of electrolytes or acids. On the other hand, latex from the *Manihot glaciovii* behaves towards coagulants like latex from *Hevea*.

One might postulate that the proteins present in *Hevea* and *Manihot* latices differ from those in *Balata* or *Funtumia*, or that other substances are present in the more stable latices which offer additional protective action. In this connection Daniel, Freundlich and Söllner[4], and Kemp[7] have recognized protective substances in *Abiurana* and *Balata* latices, which, when added to *Hevea* latex, prevent its coagulation with acids or salts. Latex from the *Ficus elastica* behaves differently from the other latices above mentioned. It gives a negative test for protein, and is flocculated but not coagulated with acids and salts.

The influence of crystalloidal serum substances in aiding coagulation was discussed by Henri[6] in his classical investigations of *Hevea* latex. He found that diluted ammonia-preserved latex which had been exhaustively dialyzed flocculated but did not readily coagulate upon addition of acids or alcohol. Dekker[5] also noted that the coagulation of dialyzed latex with acids was incomplete. On the other hand, Beadle and Stevens[1], Stevens and Rowe[15], and Noble[9] all observed that ammonia-preserved latex reacted normally towards acid after dialysis.

Henri[6] showed that the latex particles in dialyzed latex are negatively charged and coagulate on the addition of various metal salts. He also showed in a qualitative manner that the addition of various salts to dialyzed latex increases its tendency to coagulate on addition of alcohol.

The present investigation was undertaken to show the effect of electrolytes on the colloidal stability of latex in a quantitative manner and to relate these findings with the stability characteristics of separate protein fractions contained in the latex. In this way it was hoped that the mechanism of coagulation and the fundamental factors effecting latex stabilization could be more completely elucidated.

In this investigation direct recourse was had to fresh latex from the *Hevea* and other species through the courtesy of the Division of Plant Exploration and Introduction, Bureau of Plant Industry, of the U. S. Department of Agriculture, which maintains a garden tract near Coconut Grove, Florida, containing various rubber-bearing trees and shrubs.

* Reprinted from *The Journal of Physical Chemistry*, Vol. 44, No. 6, pages 788-808, June 1940.

ISOLATION AND IDENTIFICATION OF PROTEINS IN LATEX

Bishop[2] isolated three protein fractions from fresh latex serum obtained by freezing the latex to coagulate and separate the rubber particles. Protein A was separated by adding acetic acid to adjust the serum to a pH of 4.5. Protein B was isolated by saturating the filtrate from protein A with sodium chloride, and protein C was precipitated by heating the saturated sodium chloride solution on the steam bath. Bondy and Freundlich[3] separated two protein fractions, designated A and B, from centrifuged and filtered ammonia-preserved latex serum by addition of ammonium sulfate.

In the present investigation the Bondy and Freundlich procedure was followed, except that the latex was filtered through filter cel on filter paper in a Büchner funnel. A special technique was employed, which made it possible to filter either undiluted ammonia-preserved or fresh latex without recourse to the use of a centrifuge. The filtered serum was dialyzed against distilled water, using a cellophane membrane to remove coloring matter and crystalloids before precipitating the proteins.

Separation of Protein A

Saturated ammonium sulfate solution was added with stirring to an equal volume of the dialyzed serum at a pH of 6.5. After 2 hours, precipitation was complete and the supernatant liquor was decanted. The precipitate was dissolved on the filter in dilute ammonia water of pH 8.5, and reprecipitated twice. The material was then dissolved in dilute ammonia water, dialyzed simply for 48 hours in the presence of toluene, and electrodialyzed under a potential gradient of 36 volts per centimeter for 8 hours. During this time the proteinic material precipitated as a light brown flocculent precipitate, which settled to the bottom of the cell. Precipitating apparently was complete, as the supernatant liquid gave a negative biuret reaction.

Separation of Protein B

The filtrate from protein A was saturated with ammonium sulfate at room temperature. The precipitation was complete after 48 hours, and the light brown precipitate was redissolved on the filter in a dilute ammonium sulfate solution and reprecipitated twice. Final purification was accomplished through simple dialysis and electrodialysis. Electrodialysis brought about the precipitation of protein B, as was the case with protein A.

Separation of Protein C

The filtrate from protein B was subjected to simple dialysis until practically free of ammonium sulfate. It was then heated on the steam bath; when the temperature reached 60° C precipitation took place and was practically complete within 20 minutes.

It was considered possible that protein C was a heat-denatured product of protein B which had not been removed by the salting-out process. In order that this doubt might be removed, separate aqueous solutions of proteins A and B with a minimum of salt present were prepared. When these solutions were heated to 60° C and maintained at that temperature for some time, precipitation did not take place. Furthermore, aqueous solutions of protein C did not show evidence of precipitation after long periods of dialysis, as did proteins A and B.

There was also a difference in the stability of the unprotected protein hydrosols towards bacteria. Protein B hydrosol was strongly attacked by bacteria within 24 hours, whereas hydrosols of proteins A and C were not attacked for several days.

Identification of Proteins

The protein fractions were freed from electrolytes by electrodialysis, as was done by Bondy and Freundlich. Bishop, on the other hand, simply dialyzed proteins A and B, and washed protein C in warm water. The nitrogen contents of these protein fractions found by different investigators are given in Table I. It is seen that agreement is good between our results and those of Bondy and Freundlich; however, we do not agree with Bishop's results in the case of the nitrogen content of fresh latex proteins. In our work the latex was collected in Pyrex glass tubes, and was filtered immediately in an atmosphere of nitrogen in the presence of toluene. The proteins were then quickly precipitated. It is believed that these precautions largely prevented bacterial attack on the complex proteins.

Chemical analysis of protein A from ammoniated latex gave the following results: carbon, 50.67 per cent; hydrogen, 7.25 per cent; nitrogen, 13.4 per cent;

Table I

Nitrogen Content of Protein Fractions

	Nitrogen by Kjeldahl in		
	Protein A (Per cent)	Protein B (Per cent)	Protein C (Per cent)
Bishop[2] (fresh latex)	14.0-15.1	14.5-15.4	16.4-16.9
Bondy and Freundlich[3] (ammoniated latex)	13.8	15.2	
Present investigation (ammoniated latex)	13.4	14.8	14.0
Present investigation (fresh latex)	12.7	11.8	

sulfur, 0.55 per cent; ash, 1.4 per cent; oxygen by difference, 26.73 per cent. The protein A from fresh latex was found to contain 1.32 per cent sulfur and 2.26 per cent ash. The lower content of nitrogen in the proteins from fresh latex compared with those from ammoniated latex is evidence that the proteins in fresh latex are highly conjugated. The higher sulfur and ash content of protein from fresh latex also confirms this view. It appears from these and other observations that ammonia reacts with the complex proteins in fresh latex. The proteins are conjugated glycoproteins, and this also in part accounts for their low nitrogen content. Phospholipids, soaps, and other colloids are present in latex which might be carried down with the protein and be difficult to remove. These observations are recited to point out that the proteins separated from latex cannot be considered as pure substances of uniform composition but are probably mixtures which are sometimes called complexes. Their predominant protein characteristics, however, are not greatly altered by the presence of other colloidal bodies.

Color and precipitation reactions of the proteins are shown in Table II. These tests show the true proteinic nature of the fractions and serve to identify them as conjugated glycoproteins. This confirms the work of Spence and Kratz[13], who placed the insoluble protein in crude *Hevea* rubber in the same classification. Proteins from ammonia-preserved latex fail to show the ninhydrin test, whereas proteins from fresh latex show a positive ninhydrin reaction. It is well known that the α-amino group next to a carboxyl group which gives the ninhydrin

reaction is easily split off, especially by alkali treatment. Bishop[2] observed negative Molisch reactions with all three proteins from fresh latex; this result is confirmed. Molisch tests in the case of proteins from ammoniated latex, however, are positive. Bondy and Freundlich[3] obtained positive Millon's tests for proteins A and B, whereas our Millon's tests were negative for all three proteins from both fresh and ammoniated latex. The results of this investigation show that the proteins in fresh latex are changed as a result of standing in the presence of ammonia.

TABLE II

REACTIONS OF RUBBER LATEX PROTEINS

Reactions	Protein A	Protein B	Protein C
Color reactions:			
Biuret	+	+	+
Ninhydrin	−[a]	−[a]	−[a]
Xanthoproteic	+	+	+
Millon's	−	−	−
Hopkins-Cole	+	+	+
Molisch	+[b]	+[b]	+[b]
Fehling's	+	+	+
Precipitation reactions:			
Nitric acid (Heller)	+	+	−
Lead acetate	+	+	+
Mercuric acetate	+	+	+
Copper sulfate	+	+	+
Picric acid	+	+	+
Tungstic acid	+	+	−
Dichromic acid	+	+	−
Aluminum sulfate	+	+	−
Calcium acetate	+	+	−

[a] Test positive in the case of proteins from fresh latex.
[b] Test negative in the case of proteins from fresh latex.

EFFECT OF SALTS ON THE COAGULATION OF PROTEINS

A study of the colloidal behavior of the different proteins should test the validity of the protein theory and aid in determining which proteins are important as far as the colloidal properties of the rubber particles are concerned. An attempt was therefore made to determine the effect of salts on the stability of each protein hydrosol towards coagulants. A comparison of the properties of the protein hydrosols with the properties of normal and dialyzed latex is shown in Table III. Protein hydrosols A and B were prepared by dissolving the freshly precipitated proteins in a small amount of water and dialyzing the resulting solution until free of ammonium sulfate. The protein hydrosol C was prepared by simple dialysis followed by electrodialysis of latex serum to precipitate completely proteins A and B which were filtered off, leaving protein C in solution. The negative sign in Table III means that precipitation of the proteins did not readily take place.

It was not possible to show in Table III the relative effect of different salts on the coagulation of the proteins. A divalent salt such as barium chloride was found to be more effective than a monovalent salt such as sodium chloride. In some cases the addition of a small amount of barium chloride brought about the coagulation of proteins A and B without the necessity of adding a coagulant. In addition, there was a difference in the coagulating power of the organic co-

agulants,—acetone, for example, being much more effective than alcohols. In order to obtain comparable results, the amount of coagulant added was that necessary to show rapid coagulation in the presence of salt.

These observations show that the hydrosols of all three proteins are subject to a "salt effect", which acts in the direction of increasing the instability of the hydrosols on heating and in the presence of the usual latex coagulants. The experiments show also that latex is readily coagulated by acids if salts are present and the hydrogen-ion concentration approaches the isoelectric range of proteins A and B. Bondy and Freundlich[3] found the isoelectric point of protein A to be 4.5 and that of protein B to be 3.9. Addition of organic coagulants results in the coagulation of all three proteins in the presence of salts. As the salt content is reduced, more coagulant is required. In the absence of salts no coagulation occurred at a pH of 6.5 to 7.0. Heat coagulation of normal

TABLE III

EFFECT OF SALTS ON COAGULATION OF PROTEIN HYDROSOLS AND LATEX

pH of protein hydrosols = 6.5 to 7

Coagulating conditions	Sodium chloride content (Per cent)	Protein A	Protein B	Protein C	Latex
Dilute acetic acid	1.0	+	+	−	+[a]
	0.05	−	−	−	−[b]
	0.0	−	−	−	−[c]
Methyl alcohol (40 to 60 per cent)	1.0	+	+	+	+
	0.05	−	+	−	+
	0.0	−	−	−	−
Acetone (10 to 20 per cent)	1.0	+	+	+	+
	0.05	−	+	−	+
	0.0	−	−	−	−
Heating at 75° C.	1.0	+	−	+	+
	0.05	−	−	+	−
	0.0	−	−	+	−

[a] Normal ammoniated latex, pH = 10.4.
[b] Normal ammoniated latex exhaustively dialyzed and 0.05 per cent sodium chloride added. Flocculation took place in the isoelectric region.
[c] Normal ammoniated latex exhaustively dialyzed with no added sodium chloride. Flocculation took place in the isoelectric region.

latex appears to be primarily due to protein A, since protein B is not heat-coagulated and protein C is not readily coagulated with heat in the presence of salts. The heat coagulation of latex may be greatly accelerated by the addition of a small quantity of salt, as would be expected in view of the effect of salt in the coagulation of protein A. The resistance of dialyzed latex towards heat coagulation, while protein C readily coagulates, indicates either that this protein is not adsorbed on the rubber particle or that its coagulation is not sufficiently strong to bring about coagulation of latex. It was therefore concluded that the colloidal properties of normal ammoniated latex are principally governed by proteins A and B.

CHANGES IN LATEX ON DIALYSIS

In dialyzing ammoniated latex in the simple dialyzer shown in Figure 1, distilled water was passed through the apparatus continuously at the rate of 5 gallons per day. A nitrogen pressure of 6 cm. of mercury prevented dilution for the first 48 hours, and 3 cm. of pressure was sufficient thereafter. The ten-

dency for the latex to foam prevented a continuous passage of nitrogen through the system until dialysis had proceeded for 72 hours. The latex at this time was almost pure white, and behaved normally towards latex coagulants.

When dialysis was continued for 24 hours longer, latex cream formed on the membranes, and a sample of the uncreamed latex showed increased resistance towards coagulation by alcohol and organic acid. It was not, however, completely stable towards the addition of acid to a pH of about 5 over long periods of standing or when vigorously agitated. The coagulum which formed was very spongy, and closely resembled fresh latex coagulum. The rapid ad-

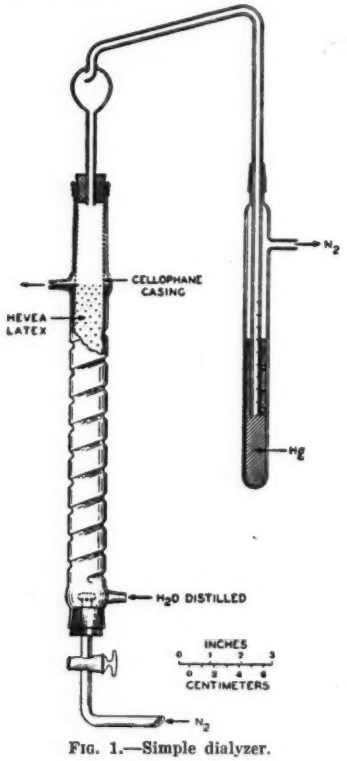

FIG. 1.—Simple dialyzer.

dition of a larger amount of acid yielded a stable acid latex. Acetone coagulated this partially dialyzed latex with practically the same ease as the undialyzed latex.

At the end of an additional 72-hour period of dialysis, the latex had creamed to such an extent that continued dialysis was not feasible. The latex was very stable towards immediate coagulation by organic acids at a pH of about 5, compared with the ammoniated latex, and when made strongly acid did not coagulate or undergo putrefaction after standing several weeks. The mechanical stability of latex, measured by flocculation on agitation, is greatly decreased by dialysis. On the other hand, the addition of ammonia or strong acids to dialyzed latex restores its mechanical stability.

The creaming of latex on membranes during dialysis has been given attention by Stevens, Dyer, and Rowe[14], who suggested that the creaming was caused by

ionic movement which carried the particles to the membrane. It was observed in the present investigation that creaming of the latex particles on the membranes always took place when dialysis had progressed sufficiently to lower the pH of the latex within the vicinity of the neutral point. The dialyzed cream on redispersion in distilled water recreams in a short period. However, by addition of a small amount of acid or alkali it forms a stable dispersion. It has been noted that creaming on the membrane does not occur when the latex is exhaustively dialyzed against dilute ammonia water having a pH of about 10.5. When the ammonia is then removed by dialysis against distilled water, creaming does not occur. Dialysis of ammoniated latex against distilled water quickly removes the ammonia, reducing the pH, which in turn reduces the electrical charge on the particles before the electrolytes have been removed. Under these conditions the particles readily cream.

Effect of Dialysis on Serum Proteins

Filtered normal ammoniated latex serum protected by several drops of toluene was dialyzed against distilled water between cellophane membranes in the convertible dialyzer shown in Figure 2. After 2 days' dialysis the serum became

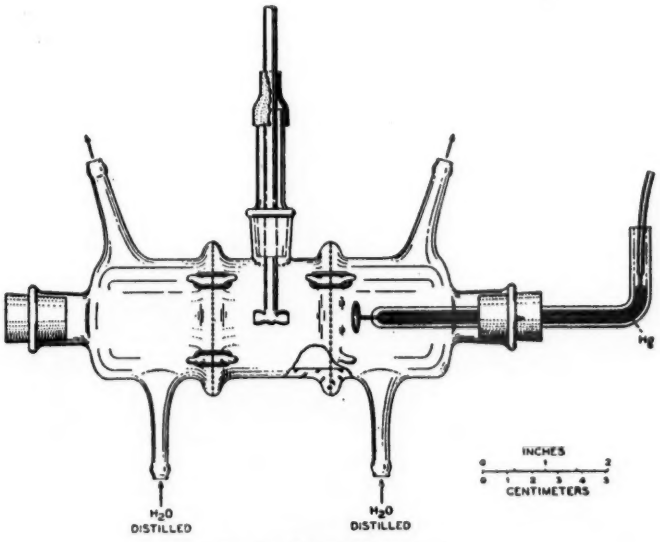

Fig. 2.—Convertible dialyzer.

almost colorless, and at the end of 5 days protein had started to precipitate and collect on the membranes. New membranes were placed in the apparatus, and dialysis was continued with a constant flow of distilled water to the end of 12 days. During this time protein continued to precipitate and the serum became very turbid, while the membranes were covered with films of protein. If dialysis is conducted against ammonia water of pH of 10.5 for example, no coagulation of proteins will occur. It appears that coagulation of protein A results from the reduction of the pH to an unstable range before salts have been removed.

To determine which protein had separated on exhaustive dialysis, a sample of the filtered dialyzed serum was mixed with an equal volume of a saturated ammonium sulfate solution. After standing 24 hours, a small amount of a colorless flocculent material separated. This was isolated; on being redispersed in a small amount of distilled water it immediately redissolved, and the solution gave negative protein tests. The half-saturated serum from the above was completely saturated by the addition of solid ammonium sulfate. Precipitation took place immediately and, after standing 24 hours, a considerable amount of protein B precipitated. These experiments show that simple dialysis brings about complete precipitation of protein A, but has very little effect on protein B. Tests also showed that protein C remained unprecipitated on dialysis.

TABLE IV

COAGULATION CHARACTERISTICS OF HEVEA LATEX

Coagulating conditions	Fresh latex	Filtered * fresh latex	Dialyzed † fresh latex	Normal ammoniated latex	Dialyzed ammoniated latex
Dilute acetic acid ‡	+ Slow §; 1-2 hr.	— Very slow §	—	+	—
Dilute acetic acid and salt ‡	+ Fast ¶	+ Fast	+ Fast	+	+
Methyl alcohol (40-60 per cent)	+	—	—	+	—
Methyl alcohol (20-40 per cent) and salt	+	+	+	+	+
Heating at 75° C	+ Slow	— Very slow	— Very slow	— Slow	— Very slow
Heating at 75° C in the presence of salt	+ Fast	+ Fast	+ Fast	+ Fast	+ Fast

* Latex filtered through filter cel, rubber-washed, and redispersed in distilled water.
† Latex exhaustively dialyzed.
‡ Acid added until pH was approximately 5.
§ Slow is 0.5 hours to 2 hours; very slow is 2 to 8 hours.
¶ Fast is less than 0.5 hour.

EFFECT OF DIALYSIS ON THE COAGULATION OF LATEX

A comparison of the colloidal properties of normal and dialyzed latex demonstrated that the "salt effect" is prevalent in normal ammoniated latex. The coagulating properties of normal and salt-free latices are given in Table IV. In these experiments an attempt has been made to correlate the observations with those made on the proteins shown in Table III to determine which of the proteins are responsible for the colloidal behavior of the rubber particles.

The slow coagulation of fresh latex in comparison with ammonia-preserved latex may be explained on the basis that the proteins in fresh latex are different chemically from those in ammoniated latex. Coagulation experiments on fresh latex proteins A and B showed that they were more stable than proteins A and B from ammoniated latex.

If freshly tapped latex is quickly coagulated by adding alcohol to 40 per cent concentration, filtering the serum, and raising the alcohol concentration of the clear serum to 80 per cent, a precipitate is formed. When this precipitate

is separated, dried and added to dilute ammonia-preserved latex, it prevents coagulation by acetic acid. This protective substance has a proteinic character and appears to be similar to the protective substance separated from *Balata* latex.

Changes in Latex Composition on Dialysis

Of the crystalloidal substances removed by dialysis, the ash components, consisting mainly of alkali and alkaline-earth phosphates, are almost completely eliminated. The total solids of exhaustively dialyzed fresh and ammoniated latex have been found to contain from 0.06 to 0.11 per cent ash, which was found to be largely phosphorus pentoxide. Rhodes and Bishop[12] found that latex contains a phosphatide in such a quantity as would account for this ash, since this substance is probably not removed by dialysis. Water-soluble organic crystalloids such as 1-methylinositol, which is present in latex to the extent of 1 to 2 per cent, would be completely removed by dialysis.

Fresh latex and ammoniated latex lose nitrogenous substances by dialysis. These substances consist in part at least of salts of amino acids, several of which have already been identified as present in latex. The decrease in nitrogen content by dialysis depends on the particular latex studied. A sample of freshly tapped latex lost 22 per cent of its nitrogen, whereas two samples of ammonia-preserved latex showed losses of 36 to 39 per cent when dialyzed exhaustively.

Most of the coloring matter in the serum is removed by dialysis, and this results in the latex becoming milky white. It was found that the serum of filtered freshly tapped latex is colorless, but turns brown quickly on exposure to air. Some lots of ammonia-preserved latex have a deep brown-colored serum, whereas others are light brown.

The total diffusible material on the total solid basis has been found to range from 8.2 per cent in the case of freshly tapped latex to 9.5 in the case of latex from the same source after 1 per cent ammonia had been added and it had stood for 2 months. The diffusate is a brown, transparent, brittle, gummy substance, and is very hygroscopic.

The rate of removal of dialyzable substances from a sample of normal ammonia-preserved latex when dialyzed in the simple dialyzer is shown in Figure 3. It is seen that dialysis is practically complete after 5 days. In this experiment the dialysis was made against ammonia water of pH 10.5, and the dialyzate was replaced periodically. The diffusate was determined by drying to constant weight.

EFFECT OF SALTS ON ALCOHOL COAGULATION OF DIALYZED LATEX

It has been shown that washed filtered fresh latex, dialyzed fresh latex, and dialyzed ammoniated latex at a pH of about 7 resist the coagulating action of alcohol to a greater extent than was the case with normal ammoniated latex. Although coagulation in the absence of salt can be accomplished by the addition of a considerable quantity of alcohol, it was definitely established that added salts of different types materially reduced the amount of coagulant. This conforms to the previous observations that a reduced salt content in the protein hydrosol greatly increases its stability. Since some salts have a greater effect than others, an attempt was made to determine the variations quantitatively. Methyl alcohol was chosen as the coagulant, and the technique developed for this purpose was as follows: The dialyzed latex of pH 7.4 was prepared by dialyzing normal ammoniated latex for 10 days against ammonia water of a pH of 10, followed by 4 days against distilled water. The latex after dialysis was ad-

justed to a total solids content of 15 per cent by the addition of distilled water. In the case where the pH was 5.4, acetic acid was added to the dialyzed latex. A sample of this latex was mixed with an equal volume of the salt solution of known molality, and the amount of alcohol necessary for coagulation was determined. This was done by first obtaining the approximate volume of alcohol which would coagulate the latex in 2 to 3 min. with mild agitation, followed by gradually increasing the amount of alcohol until coagulation was complete after 1 min. Coagulation was called complete when the alcoholic serum no longer gave indications of milkiness when rotated in an inclined test tube. The results of the experiments are given in Table V and plotted in Figure 4.

The steepness of the initial part of each curve indicates that the alcohol coagulation of latex does not result simply from the dehydration of the adsorbed

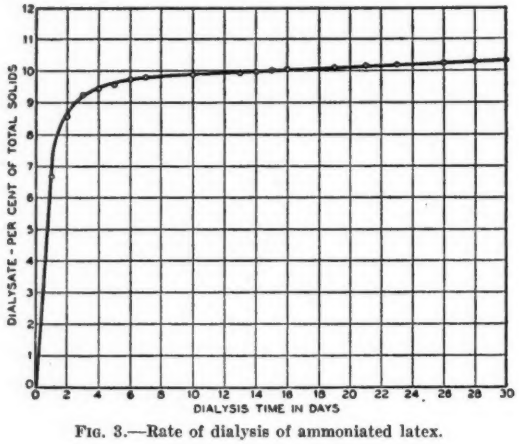

FIG. 3.—Rate of dialysis of ammoniated latex.

proteins, as generally believed. The aluminum chloride curve is unique, as it shows that small amounts of this salt behaved normally in respect to other salts, but at higher concentrations it shows very little effect. The other curves show a gradual slope towards the abscissa, the barium chloride curve striking it at a molality of 0.0475 whereas at the same molality of potassium chloride a concentration of 47 per cent by volume of methyl alcohol was required for coagulation. The greater coagulating power of divalent compared with monovalent metal salts confirms the results of Henri[6]. The abnormal behavior of aluminum chloride may possibly be related to its hydrolysis, which changes the pH of the solution. The cause of this effect, however, is not clear.

A study was made of the effect of potassium chloride, barium chloride and potassium sulfate on the coagulation of dialyzed latex adjusted to a pH of 2.5 by the addition of formic acid. In the case of potassium sulfate, the coagulation was not as sharp and complete as in the case of the other salts, making it necessary to approach the coagulation point very carefully by a very gradual increase in alcohol. Part of the latex at this end point was flocculated and the remainder coagulated, so it was necessary to determine the point where the flocculation was no longer increased by further addition of alcohol. The results are given in Table VI and plotted in Figure 5.

The maximum effect of salts on coagulation is shown in the case of barium chloride at a pH of 5.4 and 7.4, which is on the alkaline side of the isoelectric

TABLE V

EFFECT OF SALTS ON ALCOHOL COAGULATION OF DIALYZED LATEX

Salt	Salt concentration		Alcohol required for coagulation	
	pH 5.4 (Moles)	pH 7.4 (Moles)	pH 5.4 (Per cent by volume)	pH 7.4 (Per cent by volume)
KCl	0.0000	0.0000	38	95
	0.0025	0.0068	23	73
	0.0100	0.0096	18	66
	0.0200	0.0137	15	63
		0.0205		61
		0.0274		57
		0.0342		54
		0.0475		47
$BaCl_2$	0.0000	0.0000	38	95
	0.0012	0.0004	15	55
	0.0025	0.0012	11	30
	0.0050	0.0021	8	20
	0.0100	0.0029	6	15
		0.0067		13
		0.0104		11
		0.0475		0
$AlCl_3$		0.0000		95
		0.0004		62
		0.0008		49
		0.0016		48
		0.0030		78
		0.0047		84

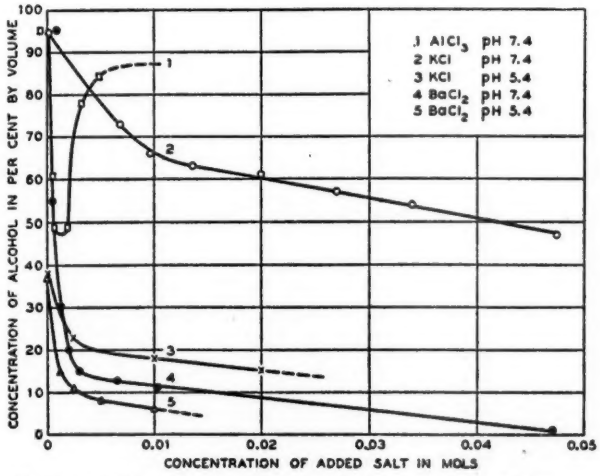

FIG. 4.—Effect of salts on alcohol coagulation of dialyzed latex.

TABLE VI

EFFECT OF SALTS ON ALCOHOL COAGULATION OF DIALYZED ACID LATEX AT 2.5 pH

Salt	Salt concentration (Moles)	Alcohol required for coagulation (Per cent by volume)	Remarks
KCl	0. -0.4	>95	Stable alcosol
	0.1-0.4	>95	Slight coagulation
	0.5	92	
	0.6	77	
	0.7	63	
	0.8	47	
	0.9	32	
	1.0	17	
	1.11	0	
K_2SO_4	0.0	>95	Stable alcosol
	0.0025	>95	Slight coagulation
	0.005	79	
	0.010	53	
	0.013	41	
	0.015	30	
	0.020	17	
	0.025	12	
	0.030	7	
	0.040	0	
$BaCl_2$	0.0	>95	Stable alcosol
	0.01-0.05	>95	Slight coagulation
	0.10-0.20	>95	Slight coagulation and flocculation
	0.30	77	
	0.40	47	
	0.50	13	
	0.55	0	

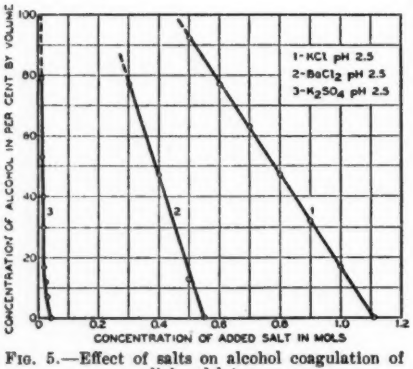

FIG. 5.—Effect of salts on alcohol coagulation of dialyzed latex.

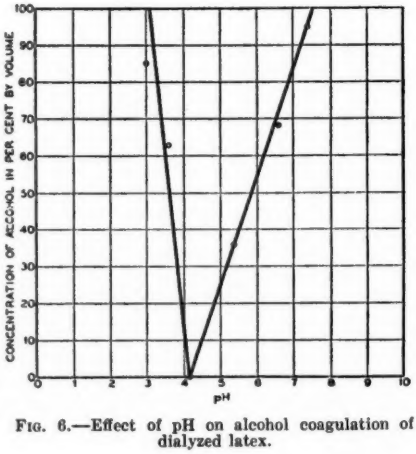

FIG. 6.—Effect of pH on alcohol coagulation of dialyzed latex.

point, and by potassium sulfate at a pH of 2.5, on the acid side. Barium chloride at a pH of 2.5 is approximately twice as effective as potassium chloride at the same pH, indicating that the chloride ions in the barium chloride are involved primarily, and that the barium ions do not enter into the coagulation phenomena. On the other hand, at a pH of 7.4 it is the barium or positive ions which effect coagulation. These data show that the divalent positive ions are more effective than monovalent positive ions when the pH is on the alkaline side of the isoelectric point, and that the divalent negative ions are more effective than the monovalent ions when the latex is on the acid side of the isoelectric state of the particles.

A study was made of the effect of pH on the amount of alcohol required for coagulation of 7.5 per cent dialyzed latex. These results have been plotted in Figure 6, and show that alcohol coagulation depends on the magnitude of the charge on the latex particles. The maximum sensitivity to coagulation is seen to be at the isoelectric point of the latex particles, which in turn is controlled by the isoelectric points of the adsorbed proteins on the particles. Evidence in favor of the conclusion that both protein A and protein B are adsorbed on the rubber particles was obtained by a careful study of the changes in the colloidal stability of a diluted dialyzed latex at various pH intervals between 1.75 and 4.9. The experimental procedure consisted in diluting 0.05 cc. of a 29 per cent total solids dialyzed latex with 3 cc. of distilled water having a definite pH, and observing the state of the rubber particles immediately upon dilution and after 3 min. agitation. It was found that maximum instability was reached at a pH of 4.15, which is approximately half-way between the isoelectric points of the two proteins. When the pH was varied to either side of this point, a definite trend towards increased stability was noted. This was more pronounced when the pH was increased rather than when it was decreased, as is seen in Table VII. The pH determinations were made with a Beckmann pH meter, using a glass electrode.

Twiss[16] has given 4.2 as the isoelectric point of dialyzed latex, determined by studying the electrophoretic movement of latex particles under various pH conditions under a microscope. He therefore showed that there is a reversal of charge on the latex particles at a pH of 4.2, whereas the present work shows that latex has its minimum stability at a pH of 4.15. The agreement of these separate investigations, using different methods, is excellent, and leads to the conclusion that the isoelectric point of latex particles lies at a pH between 4.15 and 4.2.

DISCUSSION

It has been shown in confirmation of the finding of other investigators that the rubber particles in ammoniated latex are stabilized by complex conjugated proteins. It appears that two of the three proteins present are primarily responsible for the colloidal behavior of the rubber particles. The mechanism by which they function in this capacity is intimately associated with the electrical charge they induce on the surfaces of the rubber particles. The way in which native soluble proteins of the type similar to the rubber proteins become charged and exist in aqueous solution as proteinic anions and cations may be explained on an ampholytic basis. The two rubber proteins A and B are ampholytes, as they respond to reversible precipitation by changes in the hydrogen-ion concentration of the dispersion medium. This property has been accounted for in the case of other native soluble proteins on the basis that such proteins are polybasic acids and polyacidic bases. This would imply that the rubber proteins contain in their

TABLE VII

EFFECT OF pH ON STABILITY OF DIALYZED LATEX

pH of latex	Immediately upon dilution	After 3 min. agitation
1.75	Completely dispersed	Partly coagulated; serum very turbulent
2.00	Very slightly flocculated into very small flocculi	Partly coagulated; serum very turbulent
2.50	Very slightly flocculated into very small flocculi	Partly coagulated; serum very turbulent
2.75	Very slightly flocculated into very small flocculi	Partly coagulated; serum very turbulent
3.00	Partly flocculated into very small flocculi	Partly coagulated; serum very turbulent
3.50	Partly flocculated into small flocculi	Largely coagulated; serum cloudy
3.60 *	Partly flocculated into small flocculi	Largely coagulated; serum cloudy
3.70	Partly flocculated into small flocculi	Largely coagulated; serum cloudy
3.80	Almost completely flocculated into large flocculi	Largely coagulated; serum cloudy
3.90	Almost completely flocculated into large flocculi	Almost completely coagulated; serum slightly cloudy
4.00	Almost completely flocculated into large flocculi	Almost completely coagulated; serum very slightly cloudy
4.15	Completely flocculated into large flocculi	Completely coagulated after 2 min. agitation
4.30	Almost completely flocculated into large flocculi	Almost completely coagulated; serum cloudy
4.40	Partly flocculated into small flocculi	Largely coagulated; serum very cloudy
4.55	Very slightly flocculated into very small flocculi	Partly coagulated; serum very cloudy
4.70 *	Completely dispersed	Very slightly flocculated; serum very turbulent
4.90	Completely dispersed	Completely dispersed

* Addition of a little sodium chloride brought about sharp coagulation.

molecular structure a number of the amino acid residues of the basic and acid type. The presence of these free amino and carboxyl groups results in the so-called zwitter-ion effect, which is useful in explaining the mechanism of coagulation. The actual existence of these groups in rubber proteins has been shown by Midgley, Henne, and Renoll[8]. This insight on the amphoteric nature of the rubber proteins as applied to the proteinic sheath on the rubber particle is of fundamental importance. The adsorbed protein layer on the particles, which may be continuous or discontinuous, scatters on the surface of the rubber particles numerous positive and negative charges. When the pH of the serum is on the alkaline side of the isoelectric point of the proteins, protons are lost, and the surface of the particle contains a majority of negatively charged carboxyl groups; the magnitude of the charge on the particle depends on the pH of the solution. If the pH of the serum is on the acid side of the isoelectric point, the majority of the charges are positive and the rubber particle is positively charged. The particle becomes isoelectric when the pH of the solution is midway between the isoelectric points of the adsorbed proteins on the particles, which has been shown to be at a pH of 4.15.

Normal ammoniated latex has been shown to exhibit a "salt effect", which is due not only to the original salts present but to those formed by neutralization

in the process of coagulation. This "salt effect" has a wider application than the explanation of the properties of a well-dialyzed latex. It explains the additional stability of any latex in which the salt content has been lowered to within the neighborhood of 0.1 per cent or lower. There are many different ways in which this may be accomplished: for example, repeated filtration with intermittent washing and repeated centrifuging results in latices which exhibit additional stability towards coagulating agents.

Pauli[10, 11] showed that the complete removal of electrolytes resulted in greatly increased stability of albumin towards coagulating influences. Apparently no one has satisfactorily explained the mechanism of this "salt effect". As a matter of fact, this effect has not been widely recognized.

The experiments described in this paper on the effect of salts in the coagulation of latex with alcohol bring out many interesting points. The generally accepted idea that the coagulation of latex and proteins with alcohol is solely a dehydration phenomenon must be questioned, since it has been shown that the nature and quantity of the salts present and the pH of the solution are controlling factors in the amount of alcohol required for coagulation.

Salts have their greatest effect in coagulating latex near the isoelectric state of the adsorbed proteins. This is probably because under this condition the latex particles are weakly charged and become easily discharged by bombardment of ions of opposite charge. A highly charged latex particle, on the other hand, would not be so readily discharged to the isoelectric state by ionic bombardment. The effect of adding divalent ions of opposite charge to the particles would be expected to neutralize the charge on collision more effectively than a monovalent ion. This would explain why barium chloride is more effective than potassium chloride in the coagulation of negatively charged latex particles, and why potassium sulfate is more effective than potassium chloride in the coagulation of positively charged latex particles.

Alcohol coagulation in the presence of salts, however, may be influenced by other factors, such as salt formation directly with the protein, whereby the protein becomes less soluble. The well known precipitation of proteins with heavy-metal salts is a case in point. The addition of alcohol to a protein hydrosol would be expected to influence its hydration, and it might reduce the overall charge by reducing its ionizing power. The greatest stability of the rubber proteins would be expected in water free from electrolytes and dehydrating influences, and at a pH furthest removed from its isoelectric point. This appears to be confirmed by this investigation. As the concentration of water is reduced by addition of alcohol, the amphoteric nature of the protein would be less pronounced and its electrical charge reduced.

Latex immediately after tapping does not coagulate for some time after adding acetic acid, whereas instant coagulation occurs in the case of the ammonia-preserved product. This difference appears to be due to the increase in the salt content of the ammonia-preserved product and to a greater protective power of the fresh latex protein, which is partly destroyed by bacterial action and by reaction with ammonia on standing. In spontaneous coagulation, the protective power of the proteins and associated substances apparently is destroyed by extensive bacterial action under pH conditions favorable to bacterial activity and to coagulation. It is known that native protein sols frequently become much more sensitive towards the effect of electrolytes when subjected to various treatments which change their nature. The effect of bacteria and ammonia on fresh latex is a case in point.

The complexity of the colloid chemistry of proteins and their function as protective coatings on dispersed particles is well illustrated in the present investigation. Progress in this field has been slow, since it is very difficult to control the numerous variables which enter into experiments with proteins. Knowledge is very incomplete concerning the molecular structure of proteins, and it is well recognized that the preparation of proteins of uniform composition and properties offers the greatest difficulty.

Further work in determining the effect of salts on the colloidal stability of the numerous types of proteins found in nature may be found very useful. It is well known that the solubility of certain types of proteins, such as globulins, is increased in the presence of neutral salts.

In colloid systems the electrical charges on the dispersed particles appear to be of fundamental importance to their stability. Maximum stability exists when either the positive or the negative charge is predominantly high. A wider recognition of this view should be helpful in future studies of factors which influence the stability of such systems.

SUMMARY

1. Three protein fractions have been isolated from fresh and ammoniated latex serum. The usual color and precipitation reactions have been carried out, and they place these proteins in the classification of conjugated glycoproteins. Proteins from fresh latex differ in composition from, and are less sensitive to, coagulating influences than protein from ammonia-preserved latex.

2. Coagulation tests using latex coagulants were performed on the protein hydrosols. It was found that, as the concentration of electrolytes decreased, coagulation of the proteins was inhibited, whereas coagulation readily took place when salts were present in sufficient concentration.

3. Normal ammoniated latex has been subjected to extensive dialytic treatment in specially constructed apparatus. As the ash content of the total solids from the latex approached a value of 0.1 per cent, the mechanical stability decreased and the chemical stability increased. Addition of excess acid or alkali to dialyzed latex yielded stable latices which were highly resistant to spontaneous coagulation.

4. Quantitative coagulation studies, using methyl alcohol and salts of varying types and made on dialyzed latex adjusted to various pH conditions, show that small amounts of a dissolved salt greatly aid coagulation. Considerable variation in the effectiveness of different salts was found. In acid latex of pH 2.5 the charge on the latex particles was reversed from negative to positive, and the salt effect was shown to be different from that experienced in the case where the pH was on the negative side of the isoelectric point.

5. The amount of alcohol required to coagulate dialyzed latex depends on the pH of the latex. It is shown that the amount of alcohol required for coagulation increases on each side of the isoelectric point, which was determined to be at a pH of 4.15.

6. The protective mechanism of proteins has been discussed on the basis of the electrical charges induced on the surface of the latex particles by the presence of the protein layer. The zwitter-ion effect induced by the presence of free amino and carboxyl groups in the rubber proteins is of fundamental importance in determining the colloidal characteristics of latex.

The fresh latex from the *Hevea* and some of the other types of latices mentioned in this paper were obtained from the Department of Agriculture through

the U. S. Plant Introduction Garden, Coconut Grove, Florida. The authors wish to express their appreciation for the assistance and coöperation of the Department.

REFERENCES

[1] Beadle and Stevens, *Kolloid-Z.* **13**, 211 (1913).
[2] Bishop, *Malayan Agr. J.* **15**, 27 (1927).
[3] Bondy and Freundlich, *Compt. rend. trav. lab. Carlsberg*, Sér. chim. **22**, 89-98 (1938); *Rubber Age* (N. Y.) **44**, 377 (1938).
[4] Daniel, Freundlich and Söllner, *Trans. Faraday Soc.* **32**, 1570 (1936).
[5] Dekker, *Comm. Delft* **1**, 27 (1916).
[6] Henri, *Caoutchouc & la gutta-percha* **3**, 510 (1906).
[7] Kemp, *Proc. Rubber Tech. Conf. London*, **1938**, pp. 68-79: *India Rubber World* **99**, 41 (1938).
[8] Midgley, Henne and Renoll, *J. Am. Chem. Soc.* **59**, 2501 (1937).
[9] Noble, *Proc. Rubber Tech. Conf. London*, **1938**, pp. 131-50.
[10] Pauli, *Ann. Rev. Biochem.* **3**, 118 (1934).
[11] Pauli and Valko, "Kolloidchemie der Eiweisskörper," Theodor Steinkopff, Dresden and Leipzig **1933**.
[12] Rhodes and Bishop, *J. Rubber Research Inst. Malaya* **2**, 124 (1930).
[13] Spence and Kratz, *Kolloid-Z.* **14**, 262 (1914).
[14] Stevens, Dyer and Rowe, *J. Soc. Chem. Ind.* **56**, 397T (1937).
[15] Stevens and Rowe, *J. Soc. Chem. Ind.* **58**, 116 (1939).
[16] Twiss, *Trans. Inst. Rubber Ind.* **6**, 419 (1931).

THE PROTEINS OF *HEVEA BRASILIENSIS* *

1. ANALYSIS OF A PRODUCT ISOLATED FROM DRIED LATEX

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Much work has been done on the correlation between the physical properties and the protein content of rubber latex. Weber[1] and Freundlich and Hauser[2] suggested that the rubber globules in latex were coated with protein and that this protective layer influenced the coagulation of the latex[3]. Knowledge regarding the nature and composition of the protein(s) of latex, however, is still incomplete and, with the exception of the work of Belgrave[4] and Bishop[5], and the early work of Frank[6], there have been no detailed accounts of the isolation and differentiation of the individual proteins.

Some attention must be given to the works of Belgrave and of Bishop because, apart from qualitative tests mentioned in other papers, they are the only workers who have attempted to elucidate the chemical composition of the proteins of latex. Thus Belgrave[4] obtained a single product by a method involving the use of alcohol as a rubber precipitant, while Bishop[5] isolated three products, A, B and C, from serum obtained by the freezing of fresh latex. The results, obtained by the indirect method of Van Slyke, are given in Table I.

TABLE I

VALUES QUOTED ARE IN PERCENTAGE OF TOTAL PROTEIN-N

	Belgrave	Bishop		
	I	A (acid)	B (NaCl)	C (heat)
Ammonia-N	7.7	5.65	1.62	5.0
Humin-N	0.5	0.45	0.29	0.14
Diamino-N	34.6	22.6	54.0	10.0
Non-basic-N	59.2	56.9	41.8	83.4
Total	102.0	85.6	97.7	98.5

It can be seen that none of Bishop's results agrees with those of Belgrave, nor would it appear that any combination of them would agree.

The results obtained by Belgrave are of particular interest. From 11 liters of latex (D.R.C. 38-40%) he isolated 8.5 grams of protein (N, 11.6%). This is equivalent to 1.5 gram of protein (N, 15%) per kg. of dry weight (total solids approx. 40%), which amount corresponds very closely to that isolated, under the best conditions, by the present author. Moreover, recent work by Miller[7] and by Tristram[8] has shown that the Van Slyke method gives values for basic nitrogen which may be misleading, and on these grounds the diamino-nitrogen of 34.6% reported by Belgrave might well represent a true basic nitrogen of approximately 20%, a value found by direct analysis in the present work. Table II shows the comparison between the two products.

Apart from a recent paper by Midgeley, Henne and Renoll[9], little is known of the amino-acid composition of the proteins of latex, and these workers do not mention the amounts of the various amino-acids found in the protein analyzed. The product isolated by them from rubber by fractionation with organic solvents

* Reprinted from *The Biochemical Journal*, Vol. 34, No. 3, pages 301-306, March 1940.

contained 12.5% nitrogen, and they obtained evidence of the presence of glycine, aspartic acid, leucine, proline, arginine, histidine and lysine; while cystine, tyrosine and glutamic acid were reported as being definitely absent. Such an analysis cannot be regarded as satisfactory, and it was decided that a more detailed study of the amino-acid composition might furnish valuable data on the products likely to result from degradation of the protein during various technical processes. At the same time it was hoped that comparative analyses might indicate how many proteins exist in latex.

TABLE II

	Belgrave	Author
Yield per kg. (D.R.C.)	1.5 g.	1.0–1.5 g.
Total N (%)	11.6	14.95
Humin-N (% of total N)	0.5	3.03
Basic-N (% of total N)	34.6	20.0
Ammonia-N (% of total N)	7.7	7.1

EXPERIMENTAL

The chief difficulty with regard to the preparation of one, or perhaps more than one, protein from latex lay in the fact that fresh latex itself was not available and, after experiments with various preserved products, it was ultimately decided to use air-dried films, prepared in Malaya from fresh latex, as the starting material. It was realized that drying may have caused some denaturation, but whatever the change it should not have affected the amino-acid composition of the protein(s).

The method employed was to extract the film with a borate buffer, *p*H 9.2. The dried latex was shredded into thin strips and extracted for 12 hours (including 3 hours at 50°) with 0.024*M* sodium diborate[10], to which were added 0.4 vol. of alcohol and 0.1 vol. of ether. The extract was filtered through paper pulp with a top layer of silica gel (B.D.H. Hyflo Super Cel), and the protein coagulated by acidifying to *p*H 4.5-5.0 with 10% acetic acid. The yield was found to be very variable.

In one experiment approximately 24% of the total nitrogen of the dried latex was extracted and, of this amount, about 30% was precipitated as protein-nitrogen, corresponding to 1.2-1.9 gram of protein per kg. of dried latex. An attempt was made to obtain increased yields of protein by repetition of the borate treatment after reshredding the extracted strips on smooth rolls. Much nitrogenous material was thus obtained in solution, but the amount of protein therein was negligible. Whether any protein was rendered unavailable by this latter treatment is uncertain, but it is known that mastication does, in fact, produce a change in the protein, and it may be that all, or part, of that which remained in the films was denatured on the rolls and could not, in consequence, be extracted by the borate buffer, which, according to J. W. H. Lugg (private communication), will not extract denatured protein. Various other media were tried, including solutions of LiCl, NaCl, Na_2SO_4 and $(NH_4)_2SO_4$, but none of these extracted any protein.

The protein obtained was perfectly white while wet, but on removing water by means of alcohol it darkened somewhat to a buff powder. The isoelectric point was not determined accurately, but flocculation from borate solution occurred between *p*H 4.5 and 5.0. The undehydrated product was soluble in dilute NaOH (*p*H 8.5), and was precipitated from such a solution by nearly complete saturation with NaCl (the precipitate did not redissolve on dilution),

and by one-third saturation with $(NH_4)_2SO_4$. (Bondy and Freundlich[3] isolated from ammoniated latex a protein which was precipitated from solution by one-third saturation with $(NH_4)_2SO_4$.)

Surface Films

A sample of protein which had not been extracted with alcohol and ether was dissolved in 0.05 *N* NaOH and diluted with borax to make an approximately 0.01% solution of *p*H 8.5. This solution was spread on phosphate buffer (*p*H 7.0), and examined by means of a Langmuir-Adam surface pressure balance. On compression the pressure became measurable at a surface concentration of approximately 0.4×10^{-7} gram of protein per sq. cm., and rose steadily to reach a value of 14 dynes per cm. at a concentration of approximately 0.8×10^{-7} g. per sq. cm. The film was liquid throughout. The areas observed are much smaller than those normally found for proteins[11], and furthermore all proteins hitherto examined have given gel films on compression. The behavior found here is typical of mixed films of protein and fat, and further examination showed that considerable amounts of lipin could be extracted from the protein by means of alcohol and ether. When this had been done, the protein could no longer be spread on phosphate buffer (*p*H 7.0) from borax solution. A 0.05 *N* NaOH solution was therefore diluted with 20 volumes of 75% ethyl alcohol to make an approximately 0.01% solution, from which films could readily be spread. The limiting surface concentration at which the pressure was first measurable was about 1.0×10^{-7} g. per sq. cm., and the pressure rose to 10 dynes per cm. at 1.8×10^{-7} g. per sq. cm., while gelation was observed at a pressure of 2 dynes per cm. These observations bring the latex protein into line with proteins previously studied.

Since both the lipin and protein had been extracted from the latex by what was essentially an aqueous solvent, it was thought that the lipin might contain phosphatide. Analysis showed, however, that it contained no more than a trace of P and that it consisted largely of glyceride. In one particular experiment a crude product gave 2.9 grams of lipin and 1.50 gram of protein. The lipin gave the following analysis:

N	0.07%
P	Trace
Glycerides	91.65% (fat acids 87.7%)
Unsaponifiable matter	7.14% (81.4% precipitated as digitonide)
Total recovered	98.79%

Homogeneity of the Various Samples of Protein

As stated above, the yield of protein varied widely, on occasions being as high as 1.9 gram per kg. of dried latex; and in all 11.36 grams (after thorough extraction with alcohol and ether) were obtained from 9 kg. of dried latex. In view of the large variation in yield, it was necessary to check the homogeneity of the products obtained from the different samples of dried latex. Lugg[12, 13] states that the tyrosine content of a protein may be estimated with a fair degree of accuracy (2%), and estimations of this amino-acid were accordingly carried out on the first sample of protein (0.5 gram) and on the bulk sample (11.36 grams) with the following results:

	Total wt. (g.)	Total N (%)	Tyrosine (%)	Tryptophan (%)
Batch 1	0.50	14.9	6.40	1.25
Bulk	11.36	15.0	6.40	1.35

These values suggest that the various samples of protein were of the same composition.

Analysis of the Protein

The protein was analyzed for the nine more important amino-acids, *viz.*, tyrosine, tryptophan, cystine, methionine, arginine, histidine, lysine, glutamic acid and aspartic acid, and also for amide-nitrogen by micro and semimicro methods which have been repeatedly checked, using standard proteins, by workers in this laboratory.

Amide-Nitrogen.—The protein was hydrolyzed for 3 hours with 2*N* HCl, and the liberated ammonia was estimated by (Kjeldahl) distillation into standard acid.

Tyrosine and Tryptophan.—Triplicate estimations were carried out using the colorimetric method of Lugg[12, 13].

Total Sulfur.—The method used was the alkali-fusion recommended by Bailey[19] and Lugg[13].

Table III

Analysis of Casein

Method	Wt. of protein (g.)	Glutamic acid (%)	Aspartic acid (%)
Macro (Foreman)	70	21.0	6.2
Micro modification	2.5	18.7	5.76
		19.1	5.76
Percentage recovery		90.4	93.0
		Arginine (%)	Lysine (%)
Tristram[8]	2.5	3.76	6.02
The same, applied to dicarboxylic acid filtrate	2.5	3.84	5.93
Percentage recovery, approx.		100	

Cystine and Methionine.—These were estimated by Baernstein's method as modified by Lugg[13].

Basic Amino-Acids.—(Single determination.) These were estimated by Block's method[14] as modified by Tristram[8].

Dicarboxylic and Basic Amino-Acids.—The modification of the original Foreman method[15] used in this laboratory[16] requires 20-50 grams of protein but, owing to lack of material, it was necessary to carry out the estimation on no more than 4.0 grams of protein. Trial experiments carried out on casein showed that, using 2.5 grams of protein, approximately 90% of the glutamic and aspartic acids were recovered as hydrochloride and copper salt, respectively, and that arginine and lysine could be accurately estimated in the filtrate from the alcoholic precipitation of the calcium salts (Table III).

The technique was applied to the rubber protein, and the values obtained for the dicarboxylic acids (Table IV) were given a correction which assumed that the recovery observed was the same as in the case of casein. The results of these analyses are given in Table IV; for the purpose of comparison, the limiting values for leaf proteins analyzed by similar methods[17] have been included.

TABLE IV

ANALYSIS OF LATEX PROTEIN

	Protein of *Hevea* latex		Various leaf proteins
	N of amino-acid in % total protein-N	Amino-acid as % protein (N=17% †)	Amino-acid as % protein (N=17%)
Ammonia	7.07	1.46	0.97– 1.17
Arginine	12.9 *	6.90	7.1 – 8.2
	13.0		
Lysine	6.4 *	5.68	4.6 – 6.2
	6.4		
Histidine	1.0	0.63	1.0 – 1.6
Glutamic acid	7.65	13.68	11.4 –14.0
Aspartic acid	6.5	10.5	7.9 – 8.8
Tyrosine	3.3	7.24	4.8 – 6.1
Tryptophan	1.2	1.49	2.1 – 2.4
Methionine	0.62	1.12	2.2 – 2.7
Cystine	0.70	1.02	1.4 – 2.2
Total accounted for	47.4	49.72	
% Total N in product analyzed	14.95	—	12.8 – 15.0
Total S	0.70		

* Estimation carried out on the filtrate from the Ca salts of the dicarboxylic acids.
† The N content of the latex protein has been taken as 17% for the purpose of comparison with the leaf proteins[17].

DISCUSSION

The nine amino-acids estimated represent 47.4% of the total nitrogen. Since great difficulty was experienced in the estimation of cystine and methionine, the values for these amino-acids must be regarded as minimal only.

It can be seen from Table IV that the protein has many points of resemblance with those of typical leaf proteins; this is particularly marked in the case of the diamino-acids and the dicarboxylic acids, and the similarity suggests that there may be some relationship between the proteins in the leaves and in the latex of *Hevea brasiliensis*. Samples of protein have now been isolated from the leaves of *H. brasiliensis*, and it is hoped to make comparative analyses in the near future.

Midgeley, Henne and Renoll[9] stated that the protein present in rubber did not contain cystine, tyrosine and glutamic acid. The protein analyzed by the author, however, contained 12% glutamic acid, 6.4% tyrosine and at least 1.0% cystine (calculated as amino-acids on the protein). It is realized, however, that the two proteins in question may not be identical, since it is not claimed that the protein isolated by the extraction of dried latex with borate buffer represents the whole of the protein in latex. Further investigation is accordingly in progress to find what relation the protein so far isolated bears to the whole protein(s) of latex. It has often been stated[18] that latex contains two proteins, and that on coagulation one of these (A) remains in the serum, while the other (B) is believed to be adsorbed on the precipitated rubber. If this theory be correct then dried latex will contain both A and B, and borate buffer might be expected to extract A preferentially. Crepe rubber on the other hand should contain B only. Preparations of protein from both these products are now being made by the method of Midgeley, Henne and Renoll to test this supposition by comparative amino-acid analysis.

SUMMARY

A protein has been isolated from dried *Hevea* latex and analyzed for amido-nitrogen, tyrosine, tryptophan, cystine, methionine, the basic amino-acids and the dicarboxylic acids.

The dicarboxylic acids were estimated in 4.0 grams of protein, experiments on casein having shown that, under such conditions, approximately 90% of the glutamic acid and aspartic acid was recovered as crystalline derivatives. It was also found possible to estimate arginine and lysine in the filtrate from the calcium salts of the dicarboxylic acids.

The protein is, in many respects, similar to the proteins found in leaves of other plants (Table IV).

Further work is in progress to investigate the relationship of the isolated protein to the total protein of latex.

The author wishes to thank Prof. A. C. Chibnall, who was responsible for directing the course of the research, and whose advice and criticism have proved invaluable, and Dr. G. Gee for kindly carrying out the surface film measurements.

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REFERENCES

[1] Weber, *Ber.* **36**, 3108 (1903).
[2] Freundlich and Hauser, *Kolloid-Z.* **36**, Zsigmondy Festschrift **1936**, 15.
[3] Bondy and Freundlich, *Compt. rend. lab. Carlsberg* **22**, 89 (1938).
[4] Belgrave, *Malayan Agr. J.* **13**, 367 (1925).
[5] Bishop, *Malayan Agr. J.* **15**, 27 (1927).
[6] Frank, "The Rubber Industry," London **1914**, p. 144.
[7] Miller, *Biochem. J.* **29**, 2344 (1935).
[8] Tristram, *Biochem. J.* **33**, 1271 (1939).
[9] Midgeley, Henne and Renoll, *J. Am. Chem. Soc.* **59**, 2501 (1937).
[10] Lugg, *Biochem. J.* **33**, 110 (1939).
[11] Adam, "Physics and Chemistry of Surfaces," Oxford **1938**, p. 87.
[12] Lugg, *Biochem. J.* **31**, 1422 (1937).
[13] Lugg, *Biochem. J.* **32**, 2114 (1938).
[14] Block, *J. Biol. Chem.* **105**, 457 (1934).
[15] Foreman, *Biochem. J.* **8**, 463 (1914).
[16] Chibnall, Rees, Williams and Boyland, *Biochem. J.* **34**, 285 (1939).
[17] Chibnall, "Protein Metabolism in the Plant," Yale Univ. Press. New Haven, **1939**.
[18] de Vries, *Arch. Rubbercultuur* **8**, 264 (1924).
[19] Bailey, *Biochem. J.* **31**, 1396 (1937).

THE DIALYSIS OF LATEX AND THE PROPERTIES OF DIALYZED LATEX *

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I. INTRODUCTION

Since the dialysis of latex is becoming more and more important, a brief sketch will be given here of the principle on which the process is based, together with some information on the properties of dialyzed latex.

Whereas, in the beginning, dialysis was carried out only in the laboratory, the process has slowly acquired more significance in practice. Moreover, as applied to latex, dialysis has proved useful not only for physicochemical investigation of the product but also, among other uses, as an important aid in preparing special latexes.

II. PRINCIPLE OF THE DIALYSIS PROCESS

The substance to be dialyzed is placed in a container having semipermeable walls, *i.e.*, walls which pass only particles of molecular magnitude (a few A units), while particles of colloidal dimensions (50 microns or larger) cannot pass through the wall (membrane). To carry away the substance which passes through the membrane, a current of running water is maintained on the outside (Figure 1).

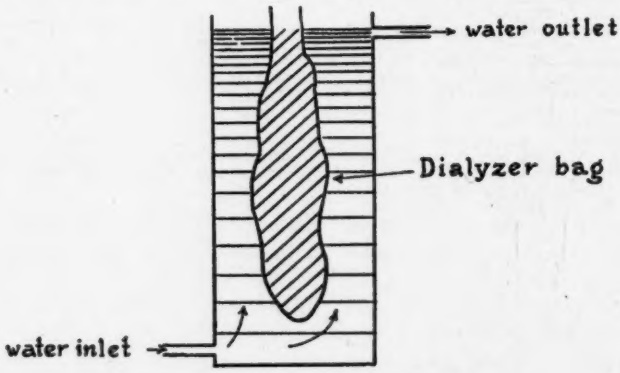

FIG. 1.—Dialysis of colloids in a collodium bag.

Formerly animal bladders, collodion films and parchment were the principal substances used for membranes. At present, however, these have been almost entirely replaced by Cellophane and similar materials, which can be supplied by modern chemical industry in a wide variety of grades and forms.

Such a Cellophane membrane can be best visualized as a three-dimensional network of cellulose molecules (Figure 2).

* Translated by Julian F. Smith for RUBBER CHEMISTRY AND TECHNOLOGY from Mededeeling No. 18 van de Afdeeling Rubber Research van het Proefstation West Java, Buitenzorg, Java. Also published in *Archief voor de Rubbercultuur*, Vol. 24, No. 2, pages 74-97 (1940).

The dialysis process may be considered primarily as a sieve effect.

Large colloidal particles are held back, while the much smaller molecules can and do pass through pores in the network by reason of their molecular motion. It is also evident that smaller molecules pass through the membrane faster than larger molecules, while at the same time the rate of dialysis depends on the concentration gradient from the inside to the outside of the membrane, on the surface area and thickness of the membrane, and on the cross-sectional area of the pores.

Aside from the sieve effect, however, there are other forces which influence passage through the membrane. These are electrical in nature.

This means that the membrane and also its pores are electrically charged (usually negatively), as is every surface in contact with an aqueous solution. As a result the membrane offers different permeabilities to positive and negative ions.

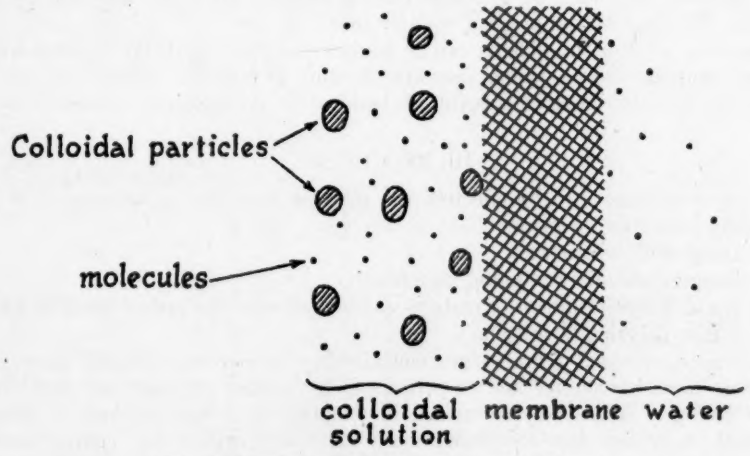

FIG. 2.—Representation of the mechanism of dialysis.

Moreover, the ions themselves differ in mobility, and these differences appear on a magnified scale in the rates of dialysis.

Clearly, however, faster dialysis, *e.g.*, of positive ions, brings about directly a potential difference, which in turn accelerates the dialysis of negative ions.

In the final calculation, the dialyzed electrical charges neutralize each other completely.

Another important complication is introduced by the fact that even colloidal particles are electrically charged and that this charge must always be equalized by its equivalent in oppositely charged ions, the socalled counter ions. These counter ions can not dialyze away. At most they can only be replaced by an equivalent quantity of other ions.

Not all the phenomena which occur at the membrane are included in this list. The mechanism of membrane action is extremely complicated, and some of its features are still being investigated.

For example, an effect which has not yet been fully explained is paste formation, or the deposition of colloids on the inner face of the membrane, which sometimes can be very troublesome.

It should be noted that the concentration gradient from the inside to the outside of the membrane sets up a difference in osmotic pressure which enables water to diffuse through the membrane from outside to inside. Of course this pressure is less at the end of dialysis than at the beginning; nevertheless considerable dilution of the colloid often takes place. Osmotic pressure is always governed wholly by molecules and ions. Colloid particles are proportionately too few in number to exert any noticeable effect.

True, it is possible, by applying counter pressure (hydrostatic or air pressure), to prevent dilution of the colloid, but this enormously complicates the dialyzer.

In principle, the same phenomena occur in dialyzing latex as in dialyzing other colloids. Rubber particles, socalled resin particles, serum proteins, and last but not least the counter ions, required by all these particles are not dialyzable. Considering the high concentration of colloidal particles, these counter ions must be present in substantial quantity. When ammoniated latex is dialyzed and ammonia is added at intervals during dialysis, the NH_4 ions are certain to take the place of the original counter ions.

Thus the ash content of latex can be made lower than by dialyzing latex which is not ammoniated or which contains sodium hydroxide. Hence the use of ammonia has still another advantage besides its preservative action.

III. PROCEDURE

If rapid dialysis is to be effected, the dialyzer must be constructed with the following principles in mind:

1. Large dialysis surface.
2. Keeping the dialysis liquid in motion.
3. Regular replenishment of dialysis water and use of the purest possible water.
4. A fast dialyzing membrane.

Moreover, elevated temperature considerably accelerates dialysis, since heat increases particle mobility and so permits faster passage through the membrane.

To obtain a large dialysis surface in proportion to the amount of dialysis material, a system has frequently been chosen in which flat compartments, separated from each other by Cellophane membranes, are alternately filled with water and with colloid.

Since special Cellophane dialysis bags are commercially available at present, it is advantageous to employ them.

Thus at the West Java Experiment Station, we constructed a 1-liter dialyzer for latex (Figure 3).

For larger quantities, we have a similar dialyzer but equipped with seven bags side by side.

This dialyzer comprises a Cellophane bag (made by Kalle A.-G. in Wiesbaden) 50 cm. long and 6.5 cm. in diameter, carried by a glass cylinder bearing a side arm, over which a rubber tube can be fitted.

At the bottom the bag is closed and weighted with a lead disk. Watertight sealing of Cellophane to glass or lead is easily accomplished with a rubber band (a piece of inner tube) tied fast with a cord. To prevent the cord from slipping off, the glass cylinder has a collar at the bottom and the lead disk is grooved around its circumference.

The Cellophane bag is placed in a large glass cylinder through which water flows constantly. A spiral glass stirrer may be rotated inside the bag.

When the bag contains too little liquid, it is compressed under hydrostatic pressure so that the stirrer cannot operate.

As long as the electrolyte concentration in the inner liquid is high, a continuous stream of water passes inward from outside, as already stated. If too much liquid enters the bag it overflows through the side arm and rubber tube to the outside, and can be collected in a separate container.

For large scale dialysis a continuous flow process is preferable. Long Cellophane bags are particularly well adapted to this purpose. Stirring of the latex is then omitted. It is advisable, however, to construct the dialyzer in such a way that pieces of coagulum forming during dialysis can be readily removed.

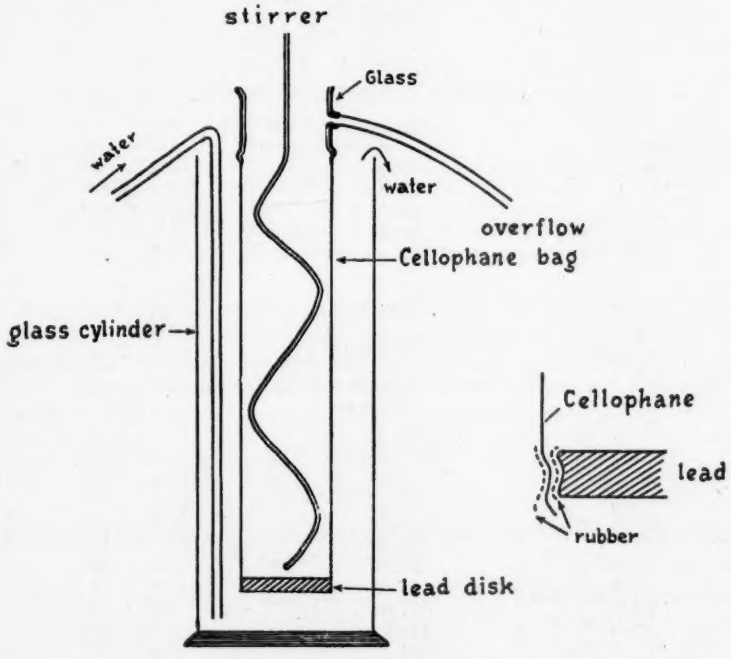

FIG. 3.—Dialyzing apparatus.

The outer liquid may be in most cases tap water or well water with low ash content.

IV. DIALYSIS OF KCl SOLUTIONS

To gain some information as to speed of dialysis, the dialyzer is filled with about 0.8 *N* KCl, and the drop in concentration is measured conductometrically.

It is clear from these figures that in the first case dialysis was somewhat faster, and the conductivity corresponding to 0.01 *N* concentration was reached in only about 12 hours, whereas in the second case this required about 15 hours, although the initial concentration was lower.

The course of change is evident when it is considered that theoretically the logarithm of the concentration and hence also the approximate conductivity decrease in proportion to time.

Thus for a given case we have the equation:

$$-dc/dt = kc$$

in which k is a definite constant independent of the apparatus, and c is the concentration at a given time.

$$dt = -1/k \cdot dc/c$$

On integrating we have:

$$t_2 - t_1 = 1/k(1n \cdot c_1 - 1nc_2) \quad \text{or:}$$
$$c_1 - c_2 = e^{k(t_2 - t_1)}$$

TEST 1

TABLE I

DIALYSIS WITH A NEW CELLOPHANE BAG

Hours	Resistance at 28° C (ohms)	Conductivity
0	6.94	88.0×10^{-3}
1	11.13	54.7×10^{-3}
2	16.35	37.3×10^{-3}
4	32.67	18.2×10^{-3}
21.30	1857	0.33×10^{-3}

TEST 2

TABLE II

DIALYSIS WITH A CELLOPHANE BAG USED 5 TIMES FOR LATEX DIALYSIS

Hours	Resistance at 28° C (ohms)	Conductivity
0	8.50	71.7×10^{-3}
1.1/6	11.53	52.9×10^{-3}
2.1/6	15.30	39.8×10^{-3}
3	21.28	28.6×10^{-3}
4.5/6	37.52	16.3×10^{-3}
6.1/6	56.40	10.8×10^{-3}
7.1/2	77.80	7.85×10^{-3}
9.2/3	138.4	4.42×10^{-3}
27	1564	0.39×10^{-3}

V. DIALYSIS OF LATEX

In dialyzing an unstable substance such as latex, care must be taken that no coagulation can occur during dialysis. Since ammonia is still the best preservative and also has the advantages set forth in Section I, it is best to keep the concentration of ammonia up during dialysis.

The ideal situation would be if the requisite ammonia could be added to the dialysis water. This involves practical difficulties, however, especially since a stream of running water must be maintained outside the membrane for the sake of rapid dialysis. For this reason we usually did not dialyze with distilled water. The tap water available was quite pure (total hardness 2.1 (German degrees), ignition residue 105 mg. per liter), so that it sufficed for most of the tests.

Usually latex ammoniated with about 5 grams of ammonia per liter was used. After 1 to 12 hours, the concentration of ammonia became so low that litmus paper was barely colored a pale blue. Our practice was to begin dialysis as early in the morning as possible. The first addition of ammonia was made about 4 P. M. (20 cc. of 20% NH_4OH) and the second addition about 9 P. M.

Usually the latex was still faintly alkaline the next morning. If further dialysis was necessary, more ammonia could be added. Conductometric control of the progress of dialysis was in this case made difficult by the fact that the addition of ammonia at intervals greatly increases the conductivity. To some extent this difficulty can be overcome by making measurements always at a time when the concentration of ammonia is very low. This can be ascertained by estimating the pH value with a test paper. After making the measurement, ammonia is added and dialysis is continued.

TABLE III

CHANGE OF CONDUCTIVITY BY DIALYSIS

Hours	Conductivity	Remarks
0	4.9×10^{-3}	Ammoniated latex
3¼	3.1×10^{-3}	Latex still alkaline
8.5	2.0×10^{-3}	Measured reaction, faintly alkaline, 20 cc. NH_3 added
19.5	0.89×10^{-3}	Measured reaction, faintly alkaline, 20 cc. NH_3 added
27.5	0.63×10^{-3}	Measured reaction, faintly alkaline, 25 cc. NH_3 added
43.1/3	0.34×10^{-3}	Measured reaction, faintly alkaline, 20 cc. NH_3 added
68.5	0.31×10^{-3}	Reaction neutral

Constant flow of water through the membrane from the outside to the inside decreases progressively the dry rubber content of latex during dialysis. As observed in our measurements, to be reported at the same time in this journal, a decrease in the dry rubber content causes an increase in conductivity. This is another reason why it is difficult to interpret conductometric data on the progress of dialysis.

TABLE IV

CHANGES IN CONDUCTIVITY, DRY RUBBER CONTENT AND AMMONIA CONTENT BY DIALYSIS

(Initial latex A 5430; DRC 37.1%; TS 39.43%; NH_3 7.32 g. per liter)

Hours	NH_3 grams per liter	DRC %	Conductivity	Remarks
0	7.32	37.1	5.66×10^{-3}	
1	5.64	35.2	5.43×10^{-3}	Dialysis continued without adding NH_3
6½	1.52	29.8	2.91×10^{-3}	Dialysis continued
12¼	0.62	27.3	1.06×10^{-3}	30 cc. NH_3 solution added after the measurement
24¾	0.42	24.7	0.45×10^{-3}	Dialysis continued without adding NH_3
28½	0.45	24.5	0.48×10^{-3}	30 cc. NH_3 solution added after the measurement
47½	0.37	22.1	0.34×10^{-3}	Dialysis finished

At the end of dialysis the total solids content was 22.36, and the pH content in the latex was 6.5.

Inward passage of water through the membrane can be prevented or even reversed in the following ways:

1. By applying hydrostatic counter-pressure to the latex (Stevens, Deyer and Rowe[1]).

2. By adding a colloid such as gelatin, casein or gum arabic to the dialysis water (Holland Patent Application 71,593).

The first case needs no explanation. In the second case the outer colloid (together with counter ions) is in competition with the inner latex as concerns fixation of water.

From Table IV it may be concluded that after about 24 hours dialysis may be considered complete. If a still greater purification effect is desired, it is best to stop the tap water dialysis after 24 hours and to continue with distilled water (the ash content of the tap water used in this case was 120 mg. per liter).

Determination of the ash offers another means for analytical control of dialysis. From this it appears that the ash content has already reached its minimum after 24 hours.

TABLE V

CHANGE IN TOTAL SOLIDS AND ASH CONTENTS IN DIALYSIS

	TS %	Ash per 100 TS	Ash per 100 latex
A. Before dialysis	33.3	2.13	0.71
After 24 hour dialysis	23.6	0.21	0.050
After 48 hour dialysis	20.8	0.36	0.075
After 72 hour dialysis	19.7	0.37	0.074
B. Before dialysis	35.6	1.32	0.47
After 24 hour dialysis	18.6	0.31	0.058
After 46 hour dialysis	16.9	0.36	0.061
C. Before dialysis	37.9	1.82	0.68
After 24 hour dialysis	23.0	0.35	0.080

It should be kept in mind that latex always contains insoluble magnesium ammonium phosphate as a result of ammoniation, and of course this compound is not dialyzable. Although the latex is stirred each time before sampling, it is still possible that more of the solid component is taken up in one sample than in another.

A much lower ash content is found in crepe prepared by acid coagulation of dialyzed latex.

VI. PROPERTIES AND DIFFERENCES OF DIALYZED AND UNDIALYZED LATEX

(See also Stevens and Rowe [3])

Differences in ash content have already been mentioned.

Aside from the inorganic components, latex also contains dialyzable organic nonrubber components.

Their removal is recognizable by a decrease in the difference between the dry rubber content and total solids content.

Removal of nitrogenous compounds lowers the nitrogen content. Usually the decrease is not large, since most of the nitrogenous compounds, *i.e.*, the proteins, are not dialyzable.

Beadle and Stevens[2] state that 20 to 25 per cent of the nitrogen in latex is removed. The difference from our results is probably due to the fact that these European investigators made their tests with a very old latex in which the protein was already partly hydrolyzed.

On the other hand Stevens and Rowe[3] obtained results more in agreement with ours.

When the outer water is not replenished in dialysis it is found to be colored distinctly yellow. Hence serum contains a dialyzable yellow or brown substance. In agreement with this, it is observed in creaming tests that the serum of di-

alyzed latex is much paler in color and may even be water-white, whereas ordinary latex serum is always colored.

When sheets are made by drying dialyzed latex on horizontal glass plates, they are much paler in color and are much more transparent than sheets made from undialyzed latex.

Dialyzed latex without ammonia is quite as sensitive to spoilage as ordinary latex, but does not develop such a foul odor when it spoils.

For creaming dialyzed latex, reference is made to our previous paper in this journal[3].

For changing the pH value by adding alkali and ammonia, we also refer to the same paper (Figures 14 and 15). From this it is evident that a given quantity of sodium hydroxide or ammonia gives a higher pH value in dialyzed than in ordinary latex, because the weak acids which act as buffers are absent.

Similarly it may be expected that on adding hydrochloric acid or formic acid, a lower pH value will be obtained in dialyzed than in ordinary latex. It appears that this is actually the case.

TABLE VI

DECREASE OF NONRUBBER CONSTITUENTS ON DIALYSIS

Latex No.	DRC %	TS %	TS—DRC	TS—(DRC/100) TS	(N/100) TS
66	38.6	41.5	2.9	7.0	0.75
66 Dialyzed	28.4	28.9	0.5	1.7	0.54
67	31.6	34.7	3.1	8.9	0.85
67 Dialyzed	22.1	22.3	0.2	0.9	0.72
69	37.2	40.0	2.8	7.0	*
69 Dialyzed	26.7	27.2	0.5	1.8	*
74	35.5	38.3	2.8	7.3	0.70
74 Dialyzed	25.1	25.7	0.6	2.4	0.60
83	31.6	34.6	3.0	8.7	0.79
83 Dialyzed 24 hours	18.2	18.6	0.4	2.2	0.62
83 Dialyzed 48 hours	16.8	16.9	0.1	0.6	0.63

* Not estimated.

The test is carried out as follows:

In each of a series of small beakers, 40 cc. latex is rapidly stirred with 10 cc. of acid of various concentrations. In the mixtures which do not coagulate, the pH value is measured with a glass electrode. It is evident that, because of coagulation, only part of the curve can be plotted.

For ordinary latex and formic acid, the measurable portion is very small, but yet large enough to give some idea as to the position of the entire curve (see Figure 4).

The coagulation limit is taken as the solution which has barely escaped coagulation after standing 2 hours.

The dialyzed latex employed in these tests had a dry rubber content of 32.3 per cent, and was used for measurements directly after dialysis without adding ammonia. Undialyzed latex, tapped the same morning, was not ammoniated and had a dry rubber content of 35 per cent.

Although our intention was to investigate coagulation phenomena more thoroughly, we may draw these conclusions from the preliminary tests:

1. The pH:acid curve is at different levels for dialyzed and ordinary latex. This had already been observed for pH:alkali curves.

2. The first coagulation range for dialyzed latex is between pH 3.9 and 5.1.

3. The upper coagulation limit for ordinary latex is at pH 5.6. We did not determine the lower coagulation limit, but according to van Harpen[4] it is at pH 3.5 for latex at a dilution of 1:9.

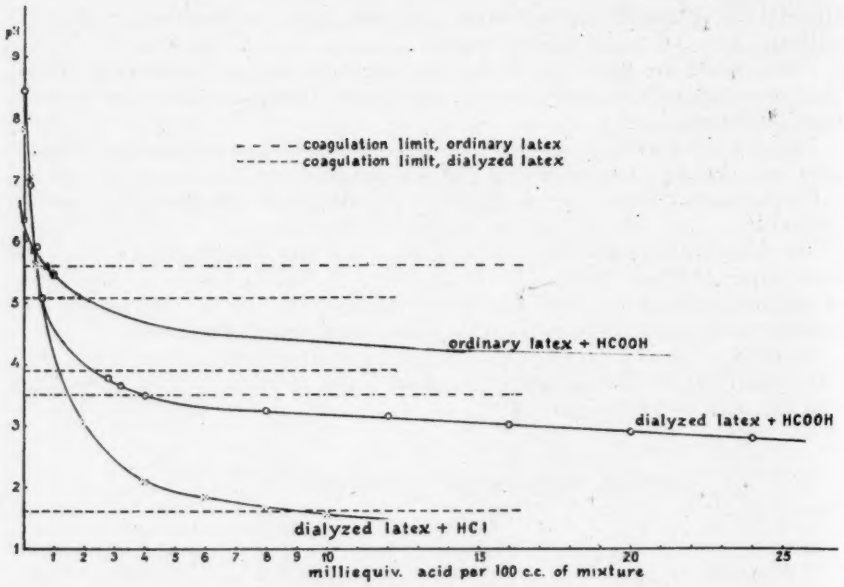

FIG. 4—Change of the pH of dialyzed and ordinary latex on addition of acids.

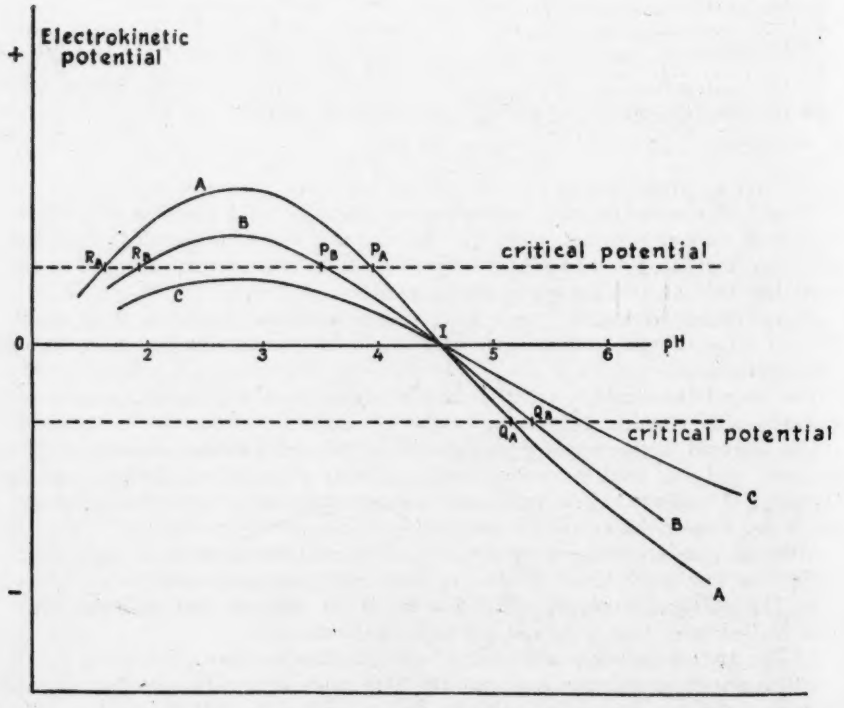

FIG. 5.—Electrokinetic potential as a function of pH.

In one of our first experiments yielding dialyzed latex, we found to our great astonishment, on attempting to coagulate the latex for a determination of the dry rubber content, that it did not coagulate. Coagulation occurred when a few cc. of sodium chloride solution, potassium chloride solution or ethyl alcohol was added with the acid.

In view of our latest experiments, this peculiar behavior becomes perfectly clear. This is the position of the pH: acid curve, and the narrow coagulation range brings dialyzed latex very quickly into the second liquid range. It may be seen from Figure 5 that dialyzed latex can be coagulated with concentrations of formic acid between 0.6 and 2.4 milliequivalents per 100 cc. of mixture and with concentrations of hydrochloric acid between 0.6 and 1.2 milliequivalents per 100 cc. These figures are quite close together.

In ordinary latex, most of the pH: acid curve is in the first coagulation range, which moreover is much wider here. Ordinary undiluted latex is not carried into the second liquid range by formic acid.

How is it then that dialyzed latex in the second liquid range can be coagulated with salts?

To answer this question, we repeated the above tests but with the addition of 4 and 8 milliequivalents, respectively, of sodium chloride per 100 cc. of mixture. This did not change the pH: acid curve, but it did change the coagulation limits.

TABLE VIa

CHANGING COAGULATION LIMITS WITH SALTS

	Upper coagulation limit (end of first liquid range) pH	Lower coagulation (beginning of second range) pH
Dialyzed latex	5.1	3.9
Dialyzed latex + 4 milliequiv. NaCl	5.2	3.3
Dialyzed latex + 8 milliequiv. NaCl	5.3 (approx.)	2.3

These results are shown in Table VIa.

The change in the coagulation limit for the second coagulation range could not be determined with certainty.

It is evident that the addition of salts widens the coagulation ranges, in fact so much so that with 8 milliequivalents of sodium chloride per 100 cc. of mixture, almost the entire pH: formic acid curve lies within the first coagulation range.

THEORETICAL CONSIDERATIONS

Although we shall return later to coagulation phenomena, we must not neglect here to present some colloid chemical considerations concerning the phenomena just described, especially since they may provide a guiding principle for further investigation.

It is probably agreed now that the charge on rubber particles depends primarily on the pH value of the medium and secondarily on the concentration of salt.

We do not, however, have any quantitative data on this point. On the basis of latex behavior, and by analogy with previous observations on other ampho-

teric colloids, it is now considered that the relation between pH and electric potential is represented by curve A in Figure 5.

On the alkaline side the latex particles are negative. At a definite pH, which in all probability is approximately 4.5, the potential is zero (isoelectric point), and at lower pH limits the potential is positive. This potential, however, passes through a maximum and then becomes smaller again.

For the sake of simplicity we assume according to Powis[6] that there is a definite critical potential above which the colloid is stable and below which flocculation and coagulation occur.

There is a critical potential for the positive as well as for the negative part of the curve. It is evident that the first coagulation range is bounded by the intersection points P_A and Q_A, and that the beginning of the second coagulation range is governed by R_A.

How will the pH: potential curve appear when salts are present? It is known that salts lower the potential, so it may be assumed that the pH: potential curve will then be given by line B, and the still higher salt concentration by line C (leaving out of consideration any change in isoelectric point caused by salts).

In case B the coagulation limits are determined by points Q_B, P_B and R_B. Thus the coagulation ranges have become wider. In case C the latex itself has ceased to be stable at all in the acid range.

We are aware that the above considerations are highly speculative and must be confirmed or amended by further experiments.

VII. PASTE FORMATION ON THE MEMBRANE

When the Cellophane bag is emptied after several hours of dialysis, it is found that a very thin layer of latex paste is deposited on the inner surface of the membrane. This paste is clearly visible at the beginning of dialysis, especially if stirring is stopped. At the end of the dialysis process, paste deposition is no longer discernible. Apparently it depends on the salt concentration gradient from the inside to the outside of the membrane.

As may be readily understood, this paste deposition hinders dialysis. For this reason we made the stirrer in a shape (spiral) so that it scraped a large part of the membrane surface as it rotated.

In the Stevens, Deyer and Rowe[1] dialysis method, inward diffusion of water through the membrane from the outside can be diminished or even entirely prevented by applying counter pressure. This, however, greatly facilitates paste deposition.

Stevens, Deyer and Rowe studied paste deposition more in detail, including the influence of substances added to the latex.

It is evident that these phenomena can be extended further. Dialysis processes, coupled with concentration of colloids on the cell walls, are constantly occurring in living plant and animal cells.

At present our knowledge of this subject is too slight to enable us to offer any explanation. We must, however, disagree with the concept offered by Stevens and his collaborators:

"During dialysis there is a concentration gradient of solute from the center of the cell to the membrane, so that the rubber particles will be subjected to a greater bombardment from the inside of the cell than from the outside, and the resultant pressure will impel them towards the membrane".

In our opinion electrical forces are involved here. That is, it has been observed that the inner liquid (latex) clearly shows a negative potential with respect to

the outer liquid. This potential can be easily measured by connecting the inner and outer liquids through two KCl:agar siphons to two similar calomel electrodes and determining potential difference in the familiar way with a Poggendorf compensation setup. Ordinary ammoniated latex was employed with tap water as the first outer liquid, followed by 0.5 *N* ammonium hydroxide and then by *N* ammonium hydroxide solution.

	Milli-equiv.
Latex: tap water	−50.5
Latex: NH_4OH (0.5 *N*)	−46.0
Latex: NH_4OH (*N*)	−39.6

From this we conclude first that latex is negatively charged with respect to the outer liquid and, second, that the potential difference falls in proportion as the ammonium hydroxide concentration gradient between the inner and outer liquids becomes smaller.

If the whole system is then allowed to stand without replenishing, the outer liquid the electrolyte concentrations inside and outside the membrane are slowly equalized, and this is accompanied by a decrease in potential difference between the inner and outer liquids. Finally the potential difference reaches a constant level at a few millivolts. Whether this small potential difference is to be attributed to imperfect equalization of electrolyte concentrations inside and outside the membrane, or to some other cause, we do not know.

From this test, however, it is perfectly evident that the inner liquid has a negative potential with respect to the outer liquid, and that the potential difference decreases whenever the electrolyte concentration gradient decreases. This potential difference in all probability is responsible for paste deposition on the membrane. Perhaps this may be conceived as resulting from pressure whereby the positively charged outer liquid forces the negatively charged rubber particles against the membrane.

VIII. ELECTRODIALYSIS OF LATEX

1. Electrodialysis in General

In electrodialysis, ordinary dialysis is combined with electrical transport of ions. An electrodialyzer is illustrated in the following diagram (see Figure 6).

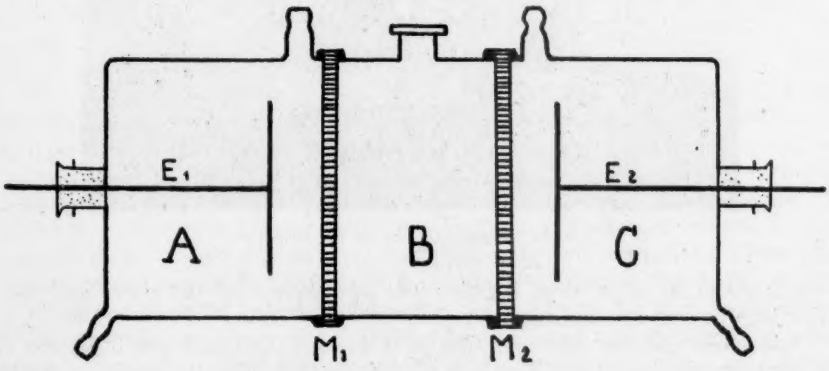

Fig. 6.—Apparatus for electrodialysis.

The dialyzer comprises three chambers, A, B and C, separated from each other by membranes M_1 and M_2. The liquid to be dialyzed is placed in chamber B, while fresh water flows constantly through A and C. By means of platinum or carbon electrodes, E_1 and E_2, it is possible to apply a potential drop through

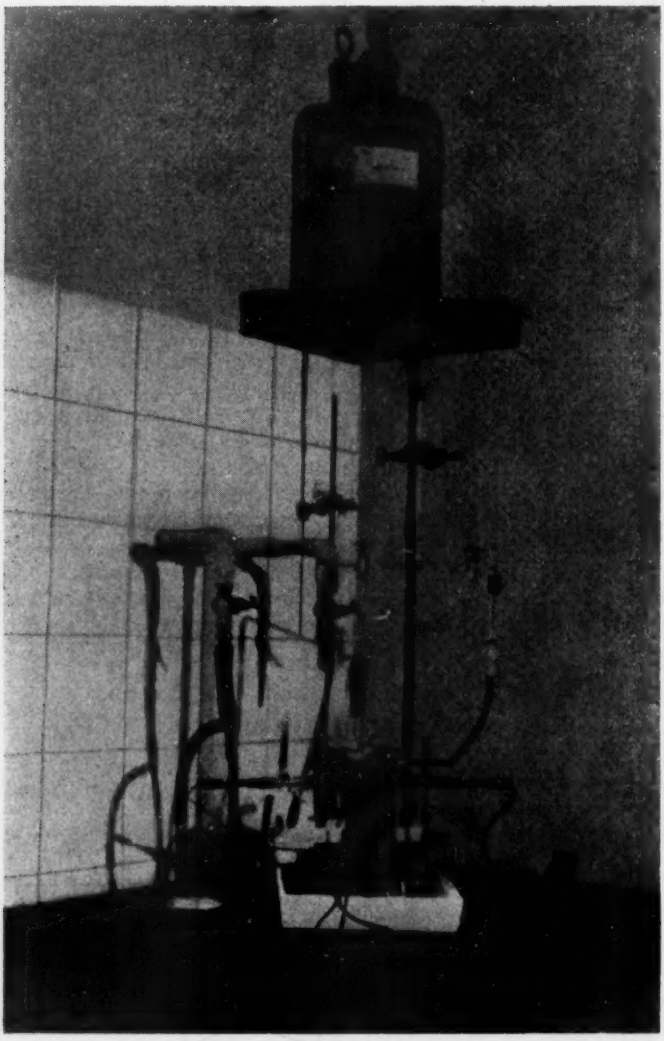

FIG. 7A.—Complete set-up for electrodialysis.

the liquid in B. As a result negative ions migrate toward the anode and positive ions toward the cathode.

Aside from the fact that ions thus pass through the membrane by reason of a concentration gradient, they are carried through also by electrical forces. Under these two influences removal of electrolytes is much more rapid than in ordinary dialysis.

In Figures 7a and 7b, a complete laboratory electrodialyzer is shown. The running water chambers are very small to provide thorough and effective rinsing. They have openings at the top to permit escape of gases liberated at the electrodes.

The circuit also includes a milliammeter, so that decreases in conductivity can be followed.

For more detailed information concerning electrodialysis, reference is made to the familiar books on colloid chemistry.

FIG. 7B.

2. CONCENTRATION EFFECTS

In connection with certain phenomena observed with latex, the concentration effect in colloids, the socalled stratification phenomenon, must be considered.

Since colloids are also electrically (usually negatively) charged, they also will migrate toward one electrode, usually the anode. In their path, however, they encounter the anode membrane which stops them, although allowing free passage of anions. Accumulation of colloid therefore occurs at the anode membrane, and since this interferes with dialysis, provision for preventing it should be made by active stirring. If stirring is neglected, the following consequences are observed. The colloid-rich liquid layer forming at the anode membrane moves downward (since it is heavier than the surrounding liquid) and collects at the bottom of the middle chamber. If conditions are favorable to this effect the bottom of the middle chamber after a few hours of dialysis will have a layer of highly concentrated colloidal solution and above it a nearly clear liquid layer.

This phenomenon, which was discovered by Pauli, and was thoroughly investigated by his collaborators Blank and Valko[7], is frequently utilized to concentrate sols, *e.g.*, serum, egg white, silver iodide and others.

3. Electrodialysis of Latex

When latex is electrodialyzed in the manner described above, the current quickly begins to decrease after electrodialysis starts. This is chiefly caused by paste deposition on the anode membrane rather than by decreasing electrolyte concentration.

Table VII

Decrease of Current on Electrodialysis, without Stirring

Voltage: 10 Volt over 9 cm.

Time (Hrs.)	Current (Milliamps.)
3.00	100
3.15	82
3.35	60
3.50	50
4.30	40

The following experiment shows that paste deposition cannot be avoided by stirring (see Figure 8).

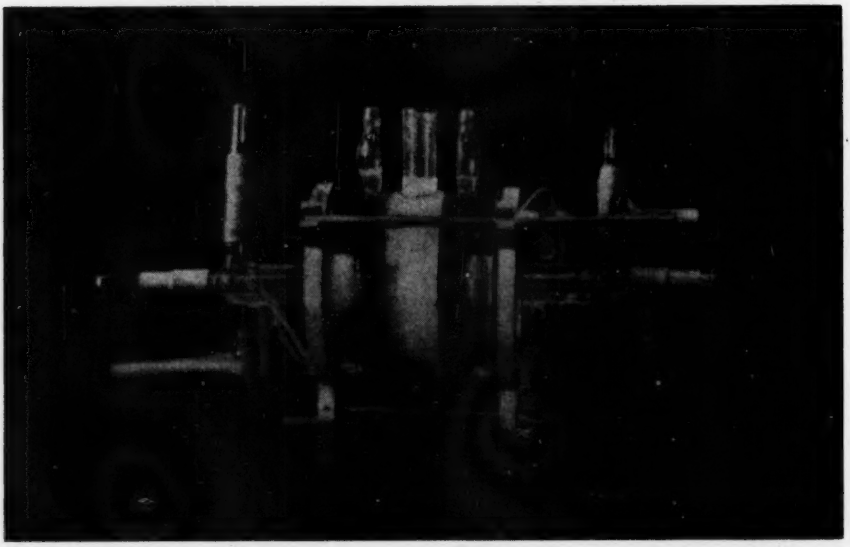

Fig. 8.—Creaming caused by electrophoresis.

Table VIII

Decrease of Current on Electrolysis, with Strong Stirring

Voltage: 10 Volt over 3 cm.

Time (Hrs.)	Current (Milliamps.)
11.15	120
11.20	90
11.30	50
11.45	34

After one-half hour the cell was emptied, paste was removed from the anode membrane, and the cell was filled again with the same latex. The current was again 120 milliamperes. Dialysis was then continued, and the current was reversed every 30 seconds. It quickly dropped to 90 milliamperes, but remained nearly constant at that level for a long time.

When the cell was emptied, both membranes were covered with a very thin film of paste.

Thus by reversing the current periodically, paste deposition can be diminished. The intervals, however, must not be too small, since otherwise the electrodialysis effect is lost.

In practice it is best to use a clockwork mechanism for reversing the current periodically. The proper interval for reversal should be ascertained by experiment. The greater the potential difference, the shorter the time interval should be.

Stratification

The phenomenon mentioned above as stratification is readily realized with latex. The process has even been patented for concentrating and purifying latex (Holland patent application 80,694, Dunlop Plantations, Ltd.).

The test is best carried out with latex which has already been dialyzed without an electric current for some time. The stirrer is then removed from the dialyzer, and the current is turned on and reversed, *e.g.*, at 15 minute intervals, to prevent paste deposition. At a potential of about 3 volts per cm., a thin layer of clear serum can be found near the bottom of the cell in about an hour.

After 1 to 3 hours, creaming is very distinct. The cream:serum interface, however, is usually less distinct than in creaming with creaming agents.

Example. Predialyzed latex (dry rubber content 17.8 per cent) was electrodialyzed without stirring. Dilute ammonium hydroxide was used as the outer liquid; distance between membranes 3 cm.; potential 10 volts. The current was reversed every 15 minutes. After 4.5 hours the resulting cream and serum were sampled.

Dry rubber content of cream.....	39.6 per cent
Dry rubber content of serum.....	4.92 per cent

REFERENCES

[1] Stevens, Deyer and Rowe, *J. Soc. Chem. Ind.* **56**, 397T (1937).
[2] Beadle and Stevens, *Kolloid-Z.* **13**, 220 (1913); Noble, *Proc. Rubber Tech. Conf. London*, **1938**, Paper No. 25.
[3] Stevens and Rowe, *J. Soc. Chem. Ind.* **58**, 116T (1939).
[4] van Gils, "Study of Creaming process", *Arch. Rubbercultuur* **23**, 256 (1939).
[5] van Harpen, *Arch. Rubbercultuur* **13**, 44 (1929).
[6] Powis; From H. R. Kruyt, "Colloids", p. 66, 85.
[7] Blank and Valko, *Biochem. Z.* **195**, 220 (1928).

HEVEA LATEX

CORRELATION OF NITROGEN AND ASH WITH TOTAL SOLIDS CONTENT *

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The purpose of this paper is to report primarily the correlation of nitrogen and ash with the total solids of *Hevea* latices. In addition it is desired to show that the nitrogen in the rubber, prepared by acid coagulation, depends on the original total solids content of the latex. A further purpose is to show that the residual nitrogen adsorbed, dissolved in, or directly associated with the rubber phase has a constant value, independent of the concentration of nitrogen in the aqueous phase. It is believed that the proper knowledge of such relations will be helpful in the preparation of better crude rubbers.

Arisz[1] made a study of the nitrogen content of latex. His work was directed to observing the change in the nitrogen content of latex as influenced by the use of various systems of tapping, both with regard to time and location of the cut. His results indicate that there is a relation between the total solids content and the nitrogen value. Using his data on tree 1 and plotting the nitrogen as a percentage of the total solids against the total solids content of the latex (Figure 1), we find that the nitrogen content of the total solids is roughly inversely proportional to the total solids content of the latex. When Arisz's data were plotted so that the nitrogen content was a percentage of the whole latex, a line parallel to the x-axis seemed to result.

Following the leads obtained from the work of Arisz, we decided to determine the nitrogen content of latex, from particular areas on our plantations, obtained by the usual tapping methods. We also decided, while these samples were available, to see how the ash varied with the total solids content of the latex, and to determine how the nitrogen would be apportioned when latices of various total solids content were coagulated.

PROCEDURE FOR NITROGEN AND ASH VALUES

The latex samples used were obtained from four areas on alternate monthly tappings. Sampling on the four areas was begun simultaneously, after each area had been through a normal rest period for one month. Twenty-eight samples were taken from each area during the month of study. One hundred and twelve samples were thus collected; of this total, one was lost during handling. The areas selected supplied latex varying greatly in total solids content. The trees supplying the latex included old seedlings, young seedlings, and a number of young buddings.

Some of the samples were preserved with ammonia and others with formaldehyde while being transported from the collecting areas to the laboratory. The weights of preservative used were always obtained accurately, so that analyses could be based on the unpreserved latex. On receipt at the laboratory, each sample was analyzed for solids content, and a portion was poured into a shallow glass dish and dried to a film in a 50° C oven. Each film was analyzed in dupli-

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 32, No. 8, pages 1072-1074, August 1940.

cate for nitrogen. The ash was determined on each film without replication. The Kjeldahl nitrogen determination was used.

As a precaution against inclusion of volatile base in the nitrogen determinations, each sample was creped thin and boiled with 0.33 per cent $Na_2HPO_4 \cdot 12H_2O$ just before analysis. The sample to be analyzed was placed in a Kjeldahl flask with 150 cc. of the alkaline phosphate solution and boiled slowly until 25 to 50 cc. of liquid remained. The nitrogen determination was then carried out on the residue in the flask. Violent agitation was practiced before pouring latex into drying dishes to assure uniform dispersion of sludge. This is a precaution essential for obtaining accurate ash figures for ammoniated latex, where an appreciable amount of inorganic sludge forms. Every effort was made to conduct each analysis in exactly the same manner, so that results would be directly comparable. The use of two preservatives is the only known source of variation in sample treatment; however, changing from formaldehyde to ammonia as preservative does not seem to make the slightest difference in ash or nitrogen

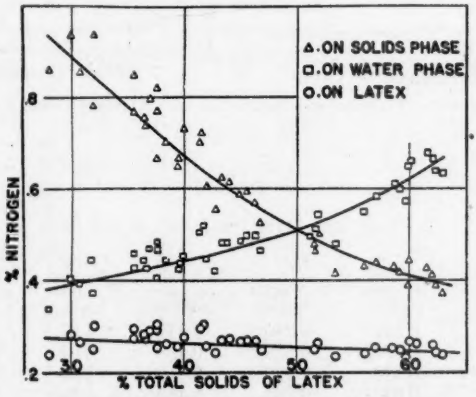

FIG. 1.—Variation of nitrogen with solids content as calculated from data of Arisz (tree 1).

analyses. Formaldehyde is probably the more desirable preservative for nitrogen content studies because of its nonnitrogenous composition.

All samples analyzed were grouped in classes according to solids content. A 1 per cent range was used for each class. Samples from 24 to 25 per cent solids content were placed in one class, samples in the range 25 to 26 per cent in another class, and so on until all samples were grouped. Averaged data for the samples are presented in Table I. The nitrogen and ash data of Table I are presented graphically in Figure 2. It is striking that curves practically identical in shape were obtained for ash and nitrogen data. The data closely follow the rule that the ash content is twice the nitrogen content. Both ash and nitrogen contents increase markedly when expressed on the solids phase, decrease appreciably when expressed on the water phase, and increase very slightly when expressed on the latex as the solids content decreases. Variation is so small for results based on the entire latex that the generalizations that the nitrogen content of latex is 0.25 per cent and the ash content is 0.50 per cent are satisfactory. The intimate relation between ash and nitrogen values indicates physiologically that the synthesis of nitrogenous material by the rubber tree is quantitatively dependent on the amount of salts absorbed by the trees.

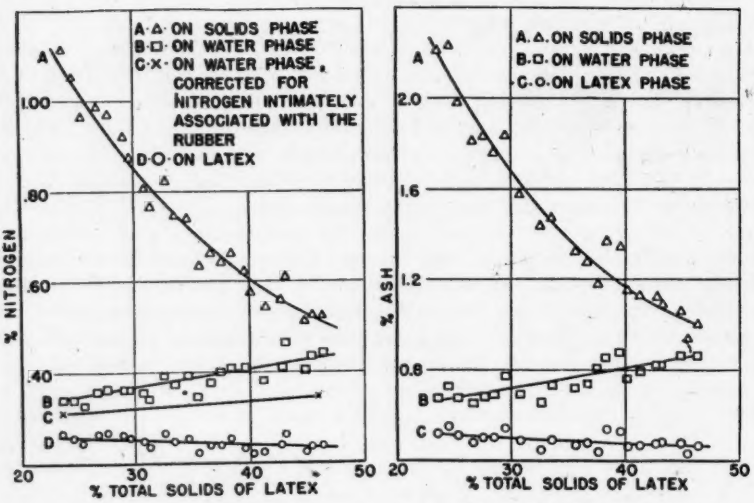

FIG. 2.—Variation in nitrogen and ash contents with latex solids content.

TABLE I

AVERAGED DATA FOR LATEX SAMPLES

No. of samples averaged	% total solids of latex	% N detd. on solids fraction	% N calcd. on latex	% N calcd. on water fraction	% ash detd. on solids fraction	% ash calcd. on latex	% ash calcd. on water fraction
3	46.30	0.522	0.240	0.447	1.01	0.47	0.87
2	45.40	0.525	0.238	0.438	0.94	0.43	0.78
2	44.89	0.513	0.228	0.415	1.06	0.48	0.87
2	43.12	0.613	0.265	0.465	1.09	0.48	0.83
8	42.68	0.561	0.239	0.417	1.12	0.48	0.83
3	41.24	0.545	0.227	0.383	1.13	0.47	0.80
2	40.16	0.578	0.233	0.385	1.15	0.46	0.77
3	39.59	0.625	0.236	0.410	1.35	0.53	0.88
10	38.42	0.663	0.255	0.414	1.37	0.53	0.86
7	37.55	0.646	0.241	0.403	1.18	0.44	0.71
4	36.61	0.663	0.241	0.380	1.28	0.48	0.74
1	35.62	0.635	0.225	0.350	1.30	0.46	0.72
1	34.63	0.740	0.255	0.395	1.35	0.47	0.71
5	33.48	0.745	0.250	0.375	1.47	0.49	0.74
2	32.58	0.825	0.268	0.395	1.37	0.45	0.66
5	31.28	0.765	0.238	0.344	1.44	0.45	0.66
4	30.75	0.814	0.251	0.358	1.58	0.49	0.70
9	29.52	0.875	0.257	0.364	1.84	0.54	0.77
8	28.48	0.921	0.263	0.367	1.76	0.50	0.70
9	27.56	0.967	0.268	0.367	1.83	0.50	0.69
6	26.71	0.990	0.265	0.360	1.81	0.48	0.66
4	25.42	0.966	0.246	0.329	1.99	0.51	0.68
5	24.56	1.053	0.257	0.343	2.23	0.55	0.73
6	23.58	1.113	0.263	0.341	2.21	0.52	0.68

NITROGEN IN CREPE

A 100-cc. portion of latex from each tapping area was accumulated daily. The accumulated samples were kept at 1.25 per cent ammonia to assure uniform preservation. At the end of each 7-day tapping period into which the tapping month can be conveniently divided, the 700-cc. portion accumulated for each plot was diluted with one liter of distilled water, treated with 10 per cent formic acid until acid to methyl red, and then treated with 200 cc. of ammonium formate buffer solution. The buffer solution, used to assure uniform acidity in coagulation, was prepared by treating 10 per cent formic acid with 20 per cent ammonia until the reaction was just acid to methyl red. One stock buffer solution was used for all samples. The latex samples, which coagulated about a minute after adding the buffer, were allowed to stand overnight and were creped and dried. The crepe samples obtained were analyzed for nitrogen in duplicate by the same procedure used for the dried latex films (Table II). The practice of boiling

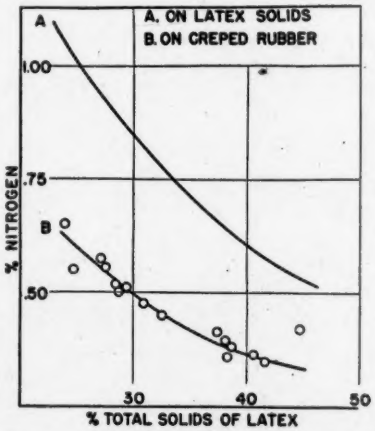

FIG. 3.—Variation in crepe nitrogen content with latex solids content.

with dilute caustic before analysis assured the removal of ammonia from the samples.

In Figure 3 the data are presented graphically for the creped samples in curve *B*. Curve *A*, a reproduction of curve *A* from the nitrogen graph of Figure 2, shows the total nitrogen present in the latex before coagulation, expressed on the solids phase. It is apparent from Figure 3 that the portion of the total nitrogen in the latex which appears in the crepe is nearly 60 per cent. As a rule, acid coagulation results in the inclusion in the crepe of all the nitrogen intimately associated with the rubber fraction, in addition to 57 per cent of the nitrogenous material normally dispersed in the latex serum.

NITROGEN INTIMATELY ASSOCIATED WITH RUBBER IN LATICES

In the paragraph just above, reference was made to the nitrogen intimately associated with the rubber fraction of the latex. This is the nitrogen so tightly fixed on the rubber particles that it cannot be washed off by repeated creaming operations. Creaming operations normally free the rubber hydrocarbon from

TABLE II

NITROGEN CONTENT OF CREPED LATEX

% total solids of latex	% N in creped rubber	% total solids of latex	% N in creped rubber
44.7	0.42	30.9	0.47
41.6	0.35	29.5	0.51
40.6	0.37	28.8	0.50
38.6	0.35	28.5	0.52
38.3	0.36	27.5	0.56
38.2	0.40	27.2	0.58
37.4	0.42	24.7	0.55
32.5	0.41	24.0	0.66

soluble serum components. To illustrate the fixed character of the residual nitrogen, a typical set of creaming data is presented. The data of Table III show nitrogen distribution in latex, serum, and cream fractions throughout four consecutive creaming operations.

TABLE III

NITROGEN DISTRIBUTION IN LATICES

Sample	Grams of sample	% total solids of sample	% N of sample (wet basis)	Grams of N in sample	N associated with 100 g. of rubber
1st serum	1287	6.53	0.228	2.930	—
2nd serum	859	2.70	0.078	0.670	—
3rd serum	625	0.763	0.029	0.181	—
4th serum	549	0.798	0.012	0.066	—
Original latex	2524	32.7[a]	0.197	4.970	0.100
1st cream	1243	60.15	0.158	1.968	0.106
2nd cream	1046	58.8	0.092	0.960	0.102
3rd cream	923	55.1	0.072	0.667	0.106
4th cream	726	57.7	0.067	0.486	0.108

[a] The latex was 39.75% in total solids content before treatment with creaming agent and dilution at the beginning of the creaming operation; the value 32.7% is for the latex as it was ready for the creaming step.

CALCULATION OF NITROGEN ASSOCIATED WITH RUBBER

An example is given to clarify the calculation procedure for those unfamiliar with creaming operations. The residual nitrogen in 100 grams of first cream is calculated as follows: One hundred grams of the first cream contains 60.15 grams of solids and 39.85 grams of water. The cream may be considered as consisting of rubber particles suspended in the first serum fraction. With the first serum analyzing 6.53 per cent solids, it follows that 100 grams of cream contain $39.85 \times (6.53/93.47)$ or 2.78 grams of serum solids. The total serum in 100 grams of cream is then $2.78+39.85$ or 42.63 grams. The nitrogen content of this serum is 42.63×0.00228 or 0.097 gram. The serum nitrogen, 0.097 gram, subtracted from the total nitrogen in the cream, 0.158 gram, leaves 0.061 gram of nitrogen associated directly with the rubber fraction of the cream. This rubber fraction amounts to $60.15-2.78$ or 57.37 grams. It follows that $(0.061/57.37) \times 100$ or 0.106 gram of nitrogen is associated with each 100 grams of rubber in the cream. This value of approximately 0.1 per cent nitrogen is in good agreement with the data of McGavack[2] determined in a somewhat different manner.

The nitrogen found in the four serum fractions and in the final cream fraction totaled 4.333 grams. Furthermore sample records show that 0.577 gram of

nitrogen was in the samples removed for analyses. The 4.333 grams of nitrogen in the final cream and the sera, combined with the 0.577 gram of nitrogen in the samples, sum up to 4.910 grams, a satisfactory accounting for the 4.970 grams of nitrogen in the original latex.

The data presented show that the latex coagulated by acid must have a varying nitrogen content in the coagulum, depending on the total solids of the original latex. Also, the data show that for uniformity it is essential to bring about this coagulation under the same conditions, *i. e.*, with the same total solids content. It may also be noticed that the nitrogen in the crepe varies more as the total solids content of the latex decreases, whereas at a total solids content of from 34 to 40 per cent the slope is not so great. Hence there will be less variation in the crepe prepared over this range than there would be in the crepe prepared from latices below 34 per cent total solids content. Rubbers at various points along this curve have been examined. The results on the characteristics of such rubbers will be reported at a later date.

ACKNOWLEDGMENT

We want to thank the Plantations Division of the United States Rubber Company for help in obtaining part of the experimental data.

REFERENCES

[1] Arisz, *Arch. Rubbercultuur* **4**, 30 (1920); **8**, 425 (1924).
[2] McGavack, *Ind. Eng. Chem.* **31**, 1509 (1939).

SEPARATION AND IDENTIFICATION OF LECITHINS FROM HEVEA LATEX *

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I. INTRODUCTION

1. NOMENCLATURE

To bring order into the chaotic nomenclature now employed for the socalled lipoid compounds has long been felt as an urgent need. In this connection, attention may be called to the decision reached in 1925 by the Committee on the Reform of the Nomenclature of Biological Chemistry, in keeping with Bloor's suggestions[1], to designate as "lipids" all fat acid esters which occur in plant or animal cells and which are soluble in alcohol and ether, and insoluble in water, and to include substances which can form esters with fat acids. Bloor's classification distinguishes:

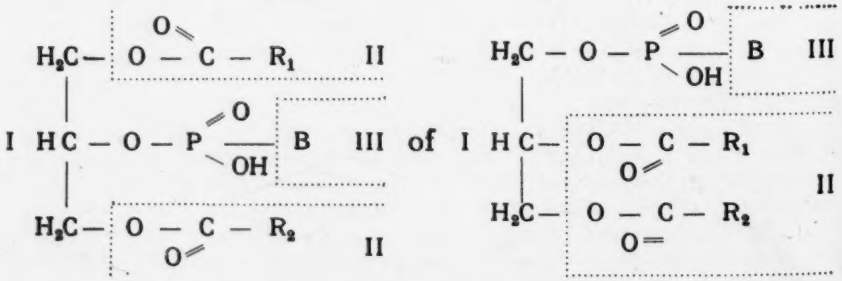
(a) *Simple lipids, i.e.,* esters of fat acids with various alcohols (fats, waxes).

(b) *Compound lipids, i.e.,* esters of fat acids with alcohols linked to a third component. These are subclassified as: (1) phospholipids (lecithin, cephalin); (2) glycolipids containing sugar and nitrogen but no phosphorus; (3) aminolipids; (4) sulfolipids.

(c) Lipid derivatives formed by hydrolysis of compounds in classes *a* and *b* (fat acids, higher alcohols, sterols).

The scant attention received by the International Committee's recommendations is most clearly illustrated by the fact that names in confusing variety persist in the literature, *e.g.,* lipoids, lipins, chromolipins, lipoins, liposes, etc., and numerous investigators still cling to these arbitrary names. The term lipoids, which, according to Overton[2], designates a fatlike substance occurring in animal or plant cells and soluble in the usual solvents for fats, has proved to be particularly convenient. According to this definition, lipoids thus coincide in a general way with Bloor's "compound lipids". It is these compounds and particularly the phospholipids or "phosphatides" (including lecithins) with which this paper is concerned.

Lecithins which are related to cephalins may be represented chemically by the following general formulas:



* Translated by Julian F. Smith for RUBBER CHEMISTRY AND TECHNOLOGY from Mededeeling No. 17 van de Afdeeling Rubber Research van het Proefstation West Java, Buitenzorg, Java. Also published in *Archief voor de Rubbercultuur,* Vol. 24, No. 2, pages 58-73 (1940).

Composed of glycerophosphoric acid (**I**), fat acids (**II**) (palmitic, stearic, arachidic, oleic, linoleic, and linolenic acids are the members of this group commonly found in the phospholipids) and a base (**III**), the lecithins with the choline radical as B and the cephalins with the cholamine radical as B are always amorphous compounds which, aside from hydrolysis by enzymes, are easily broken down by acids, alkalies, light, air, heat or moisture into their three principal constituents. This confirms once more that the instability of lecithins is an important factor in isolating these compounds.

2. Literature Survey

The presence of lecithin in *Hevea* latex was first recorded by Belgrave and Bishop[3] in a microscopic examination for detecting resins in *Hevea* latex. Frey-Wyssling[4] also found a "lipoid" which he considered to be a "fatlike ester of phytosterol with fatty or other high molecular acids". The presence of lecithins in latex was also mentioned by Beumé-Nieuwland[5].

Special attention, however, is merited by the comprehensive research of Rhodes and Bishop[6], who were able to isolate "lipins" in considerable quantities from latex. The procedure described by them is approximately as follows:

About 1.5 liter of latex is poured in a thin stream into 3.5-4 liters of ethyl alcohol. The coagulated rubber is quickly filtered with suction, and the filtrate is evaporated in a vacuum at 40° to about 300 cc. After standing in a refrigerator 5 or 6 days, the milky solution obtained is extracted with ether in a separatory funnel, and the ether extracts are evaporated. In this way an extremely small daily crop of the desired substance can be obtained. It is described as "a solid, transparent, golden yellow" substance. By following this procedure 52 times, which took nearly 3 months, Rhodes and Bishop were able to obtain no less than 151.6 grams of this ether-soluble product from 72.8 liters of latex. Thus they were able to estimate the average lipin content of latex as 0.2 per cent.

None of the publications cited above presents any positive proof that the products designated as lipins or lipoids were actually lipids. Only Rhodes and Bishop[6] analyzed the product which they isolated. Summarizing the results of their analysis, we find the following composition:

	%
Nitrogen	0.59
Phosphorus	1.72
Fat acids	71.00
Unsaponifiable	1.10
Sugars	10.00
Ash	5.35

By extracting the raw product with hot acetone these investigators obtained a residue with substantially higher nitrogen and phosphorus content, *viz.*, 0.88 and 2.56 per cent, respectively.

The free fat acids obtained from the raw product by alkaline hydrolysis yielded 95 per cent of liquid (unsaturated) and 5 per cent of solid (saturated) fat acids by the familiar lead salt and ether separation method of Varrentrop[7].

From these analytical results, coupled with the fact that the golden yellow ether-soluble product gives a purple-red color with concentrated sulfuric acid and a little sugar (Pettenkofer reaction), Rhodes and Bishop concluded that the product prepared by them must belong to the "ill-defined class of fatty bodies called lipins". The presence of a comparatively large proportion of sugars (10 per cent) is also in good agreement with observations of other investiga-

tors to the effect that lipids isolated from plants may contain as much as 16 per cent of sugars, from which the lipids can be separated only with difficulty or not at all. This explains why determinations of the nitrogen and phosphorus contents in plant lipids are always much too low (theoretically the phospholipids (lecithins) contain about 1.8 per cent nitrogen and about 4 per cent phosphorus).

This publication may be considered as supplementing the work of Rhodes and Bishop in a manner which we believe to be essential. The primary object of our investigation was to ascertain whether the lipins described by these investigators are actually phospholipids, that is, whether the nitrogen and phosphorus in this product are actually derived from choline (cholamine) and glycerophosphoric acid, respectively. During the research we found means to isolate lipids by a simple and rapid procedure. Attention is also directed to the identification of mixed fat acids liberated by hydrolysis.

II. METHOD FOR PREPARING PHOSPHOLIPIDS FROM LATEX

In clarifying latex with a De Laval centrifuge (separator), the important observation has repeatedly been made that the paste thrown against the centrifuge bowl wall is comparatively rich in brownish yellow oily slime and also contains inorganic salts and other components. A preliminary test indicates that this oil is in all probability a lipid, and specifically a phospholipid, since it apparently contains phosphoric acid. This observation alone seems to offer sufficient incentive for investigating more thoroughly the chemical composition of this phospholipid, particularly since the phosphatidic raw material is so easily obtained, *e.g.*, from the waste (centrifuge mud) in latex concentrating establishments. This is in contrast with what has just been said concerning the Rhodes-Bishop method.

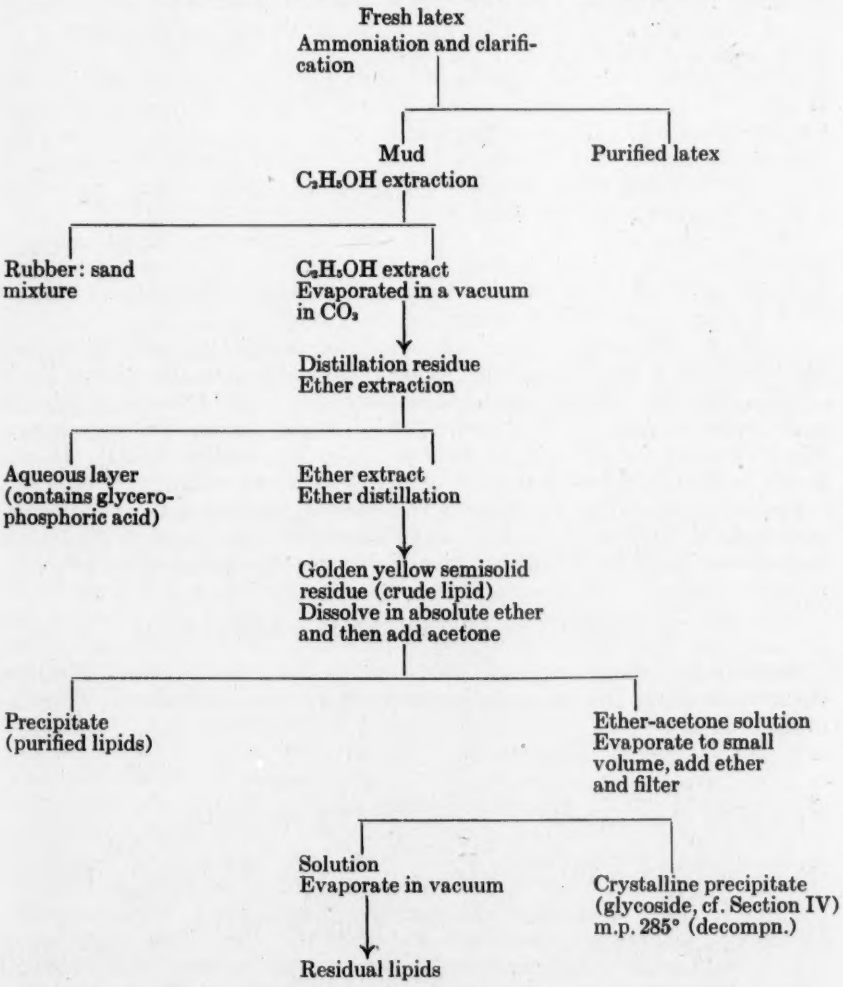
Undoubtedly our method of preparation has one disadvantage which is directly related to the instability of phospholipids in acid or alkaline media; that is, ammoniated latex is used for clarification and, obviously, ammonia is not without an effect on lipids. However, this difficulty can be largely overcome by carrying out the procedure as rapidly as possible, with particular attention to the rapid removal of ammonia from the centrifuge mud (latex which has not been ammoniated can be clarified without any difficulty[8], and gives substantially better yields). We shall take up this point further on, merely noting here that preparation of phospholipids need not take longer than 10 hours.

Various preliminary tests led to the following procedure, which is very convenient to carry out (cf. procedure I):

Fresh latex (100 liters) immediately after adding ammonia (3 grams or less per liter of latex) is clarified in a De Laval centrifuge. The mud thrown against the bowl wall is collected together with latex remaining in the bowl, and mixed with sufficient sea sand to form a paste which must not be too thick (sand prevents formation of a compact impermeable rubber coagulum which, unlike the porous rubber:sand mixture, makes effective EtOH extraction impossible. This paste, which may be saponified if necessary, is added in small portions with rapid mechanical stirring to 5 liters of 96% ethyl alcohol preheated to about 40° C. After adding all the material, the mixture is filtered in a Büchner funnel, and the precipitate is again extracted twice with the same quantity of alcohol. Passing carbon dioxide into the alcoholic solution during extraction is helpful. The yellow extracts are combined and evaporated in a vacuum in an atmosphere of carbon dioxide to a volume of 200-300 cc., keeping the boiling point below 50° C in every case. The resulting pale brown concentrate appears

to contain a thick golden yellow oil which is readily isolated with peroxide-free ether (glycerophosphoric acid can be detected in the residual aqueous layer by the method described in Section III, 1). The ether solution is dried over anhydrous sodium sulfate and the ether is distilled off, first at ordinary pressure and then (for removal of residual alcohol) in a vacuum. The residue, which will

PROCEDURE I: PREPARING PHOSPHOLIPIDS FROM LATEX



be designated as "crude lipids" is a golden yellow substance of buttery consistency. The average yield is 15 grams.

Whereas in the Rhodes-Bishop method no less than 200 grams of "lipins" can be prepared from 100 liters of latex, it appears from the discussion above that the "clarification" method yields only 15 grams of this product from the same quantity of latex. In our opinion, however, this should not be considered as a

disadvantage of the method just described. Aside from the possibility of substantially increasing yields by repeated clarification, the raw material (centrifuge mud) ceases to be a worthless waste product, merely separated to improve latex quality.

Since our product has the same properties as the Rhodes-Bishop "lipin", we consider it highly probable that the procedure described isolates the same lipids. The following method gives satisfactory purification of the crude lipids (see schematic Procedure I). The substance is dissolved in the least possible quantity of absolute peroxide-free ether and is filtered through a folded filter to remove impurities which apparently are always present (these remain as a gelatinous film on the filter and apparently contain the same glycoside, decomposing at 285°, which is described in Section IV and is obtained by recrystallization from ethyl alcohol). The clear pale brown filtrate is then added drop by drop, with mechanical stirring, to about 1 liter of absolute acetone saturated with CO_2. The resulting white flocculent precipitate is rapidly filtered off, washed with anhydrous acetone and dried in a vacuum desiccator in the dark.

About 5 grams of purified lipid can be obtained in this way from 15 grams of crude lipids. The purified product, which is colorless at first, soon takes on a brownish tint. It is more solid in consistency than the crude lipids, and in outward appearance can best be compared to "gums".

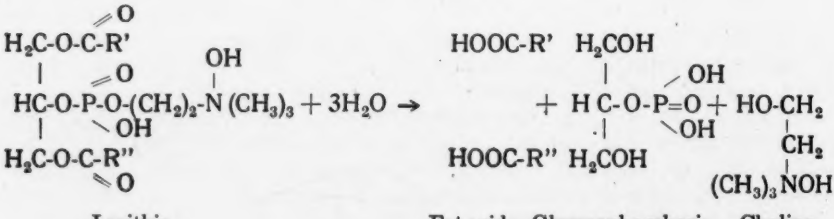
As for the yellow ether-acetone solution, distillation yields a dark thick syrup which contains a white crystalline substance in addition to the residual lipids.

This crystalline product, which seems to be only slightly soluble in ether, is easily separated from the highly ether-soluble residual lipids. The properties of this interesting material will be discussed later (see Section III, 1). It may merely be mentioned here that it can be identified as a glycoside (see Section IV).

The crude as well as the purified and residual lipids give the phospholipid color tests of Cassanova[9], Siedler[10] and Pettenkofer (see Section I, 2). In the next section it will be shown that these lipids actually contain phospholipids.

III. ANALYSIS OF PRECIPITATED PHOSPHOLIPIDS

Methods for analyzing phospholipids are all based on hydrolysis, breaking down the molecule into fat acids, glycerophosphoric acid and choline, according to the equation:



Lecithin — Fat acids — Glycerophosphoric acid — Choline

This complete hydrolysis is easily effected, and in particular choline is very readily split off even by dissolving lecithin in ethyl alcohol at 60-70° C or by allowing an ethyl alcohol-lecithin solution to stand for half an hour at ordinary temperature[11]. This may be attributed to the extreme instability of lecithins.

1. Qualitative Analysis

In qualitative analysis as applied to the "crude phosphatides" described above, we employ a method described by Fourneau and Piettre[12] and set forth in Procedure II below. The original method was improved by slight modifications.

A solution of 10 grams of crude phospholipids in 25 cc. of absolute methanol is saturated with dry hydrogen chloride gas at 0° C and heated 1 hour at 50° C, then to 75° C when escape of hydrogen chloride gas through the condenser has practically ceased.

On cooling the mixture a white crystalline substance melting at ±131° C precipitates from the resulting dark solution. This substance shows very distinctly some of the color tests for phytosterols. We shall return to this topic further on (see Section IV).

The filtered methanol-hydrogen chloride solution is poured into 500 cc. of water and extracted with ether. The ether extract and the aqueous hydrogen chloride layer are analyzed separately as follows:

After washing with dilute sodium bicarbonate solution the ether extract is dried and evaporated. The residue containing methyl esters of fat acids yields a brown oily substance when saponified with dilute potassium hydroxide. This product apparently consists of mixed saturated and unsaturated acids. The two groups are separated from each other by the familiar Twitchell method[13].

More detailed analysis of the liquid fraction containing unsaturated fat acids is carried out as described by Hazura[14] (see also Frahm and Koolhaas[15]), who oxidized unsaturated fat acids to the corresponding hydroxy acids with alkaline potassium permanganate. In this way we were able to isolate two hydroxy acids, namely, dihydroxystearic acid (m.p. 131°) and sativic acid (m.p. 175°), formed respectively from oleic and linoleic acids.

As for the solid (saturated) fat acids separation was effected by fractional crystallization successively from 100, 90 to 70% ethyl alcohol[16], a method involving exceptionally serious losses of fat acids. Nevertheless this method permitted separation of arachidic, stearic and palmitic acids in adequate quantity, and it was possible to identify the acids by their melting points (73, 69 and 61°) and by their mixed melting points (with acids prepared by other methods)[18].

Analysis of the aqueous hydrogen chloride layer was carried out as follows[12]:

To remove most of the hydrogen chloride the solution is evaporated to dryness in a vacuum, and the residue is dissolved in 50 cc. of water.

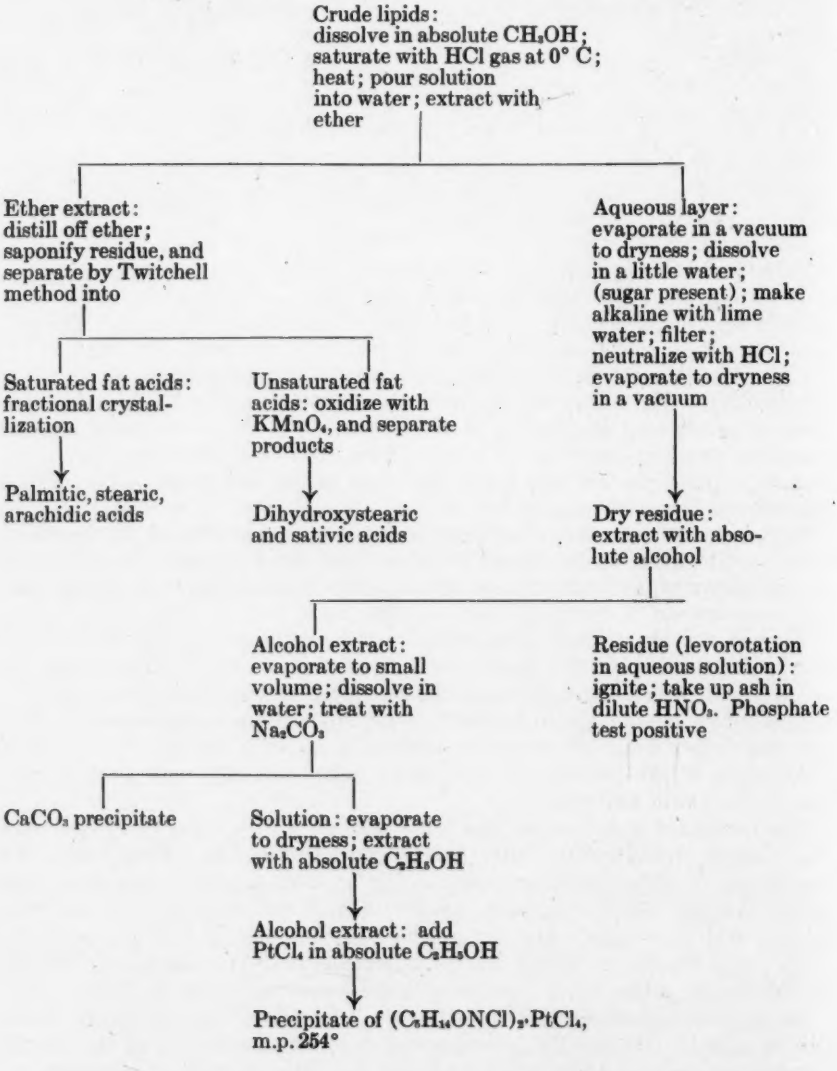
A sample of this aqueous solution shows sugars not only with Fehling solution but also with Luff reagent.

The remainder of the solution is made alkaline with calcium hydroxide solution, filtered through Norit after being heated just to the boiling point, and neutralized (to phenophthalein) with *N* HCl. After vacuum evaporation, the neutral solution yields a brownish residue which is also dried in a vacuum over sulfuric acid over night. The dry residue thus obtained is extracted with absolute ethyl alcohol in which choline hydrochloride and calcium chloride are readily soluble, while calcium glycerophosphate remains in the residue.

To remove calcium chloride from the alcohol extract aqueous sodium carbonate is added. The solution is evaporated to dryness, after which the residue is taken up again in absolute ethyl alcohol and filtered; calcium carbonate remains on the filter, while choline hydrochloride passes into the clear filtrate. This filtrate, which is concentrated and if necessary purified by boiling with Norit, gives with a concentrated platinum chloride solution in ethyl alcohol an orange precipitate of $(C_5H_{14}ONCl)_2 \cdot PtCl_4$, melting at 226°. After a single re-

crystallization from dilute alcohol it yields fine orange crystals, melting at 254° C. The platinum content of this product is 31.89% (calculated 31.68%). We were unable to detect cholamine (derived from cephalins if present) in the choline fraction.

PROCEDURE II. QUALITATIVE ANALYSIS OF CRUDE LIPIDS


Crude lipids: dissolve in absolute CH_3OH; saturate with HCl gas at 0° C; heat; pour solution into water; extract with ether
Ether extract: distill off ether; saponify residue, and separate by Twitchell method into
Aqueous layer: evaporate in a vacuum to dryness; dissolve in a little water; (sugar present); make alkaline with lime water; filter; neutralize with HCl; evaporate to dryness in a vacuum
Saturated fat acids: fractional crystallization
Unsaturated fat acids: oxidize with $KMnO_4$, and separate products
Palmitic, stearic, arachidic acids
Dihydroxystearic and sativic acids
Dry residue: extract with absolute alcohol
Alcohol extract: evaporate to small volume; dissolve in water; treat with Na_2CO_3
Residue (levorotation in aqueous solution): ignite; take up ash in dilute HNO_3. Phosphate test positive
$CaCO_3$ precipitate
Solution: evaporate to dryness; extract with absolute C_2H_5OH
Alcohol extract: add $PtCl_4$ in absolute C_2H_5OH
Precipitate of $(C_5H_{14}ONCl)_2 \cdot PtCl_4$, m.p. 254°

The residue, which is insoluble in absolute ethyl alcohol and contains calcium glycerophosphate, is dissolved in water, decolorized with Norit and treated with 25% lead acetate solution. The resulting precipitate of lead glycerophosphate is filtered off, washed with cold water and decomposed into lead sulfide and glycero-

phosphoric acid by being suspended in dilute barium hydroxide solution and treated with hydrogen sulfide so that barium glycerophosphate remains in solution. The mixture is then evaporated in a vacuum, and purification by means of the lead salt is repeated several times. After vacuum evaporation, barium glycerophosphate can be further purified by precipitation with ethyl alcohol, filtration and redissolving in water, this treatment being repeated as often as necessary. Thus a clear solution of the barium salt is finally obtained, which shows a slight levorotation[17]. When the barium salt is calcined at red heat it yields, with carbonization, a residue showing a distinct reaction for phosphates.

In summary it may be concluded from the discussion above that the crude lipids comprise a mixture of lecithins, contaminated with glycosides and combined with glycerophosphoric acid, choline and oleic, linoleic, palmitic, stearic and arachidic acids. In addition to these a compound which gives some of the phytosterol color tests has been detected in the crude lipids.

2. Quantitative Analysis

Both the crude and the purified lipids were analyzed.

The phosphorus content was determined by igniting the sample with a mixture of sodium nitrate and sodium carbonate to separate phosphate quantitatively as magnesium pyrophosphate in the ignition residue.

The nitrogen content was determined by the Kjeldahl method.

Fat acids were determined by the method described by E. H. and A. Winterstein[11], though somewhat modified by us. About 1 gram of phosphatide is boiled for 12 hours in 100 cc. of 0.25 *N* HCl under a reflux condenser. (It is helpful to dissolve the weighed phosphatides first in as little ether as possible. This ether solution gives with the required amount of hydrogen sulfide, on shaking, an emulsion which is then boiled. Thus the material to be purified is brought into intimate contact with hydrogen chloride, which substantially shortens saponification time). After cooling, the mixture is extracted with peroxide-free ether, which dissolves the liberated fat acids. These are freed from any other components which may be present by dissolving the dry ether extract in 1 per cent potassium hydroxide, filtering the solution and reprecipitating the fat acids from the filtrate, after which they are extracted again with ether. In our case this treatment removed not only the crystalline substance melting at 131°, as previously mentioned, but also a very small quantity of a rubber-like substance outwardly resembling caoutchol[19]. The ether solution is then washed with water, dried over sodium sulfate and evaporated. The residue is heated a short time at 100° C, and dried to constant weight in a desiccator.

In this way we found in the crude lipids: phosphorus 1.58, nitrogen 0.54, fat acids 84.1 per cent.

The purified lipids contained: phosphorus 2.35, nitrogen 1.05, fat acids 61.3 per cent.

IV. PROPERTIES OF THE PRECIPITATED GLYCOSIDES

In Section II, the unexpected crystallization of a white substance was described. By recrystallizing from ethyl alcohol it gave rosettes of colorless crystals (see Figure 1). At about 250° C these crystals turn brown, at 270° C they begin to sinter but do not melt until 285° C and then with decomposition. The substance is insoluble in water, acid or alkali and only very slightly soluble in organic solvents at ordinary temperature. The compound contains no other elements than carbon, hydrogen and oxygen; its molecular weight (micro-Rash method) is 555.

Of the color tests for phytosterols[20] only those of Salkowsky, Liebermann-Burchardt, Mack and Tschugajew were positive. Other phytosterol tests (Rosenheim, Brueckner, Tartelli-Jaffa and the tests for C:C double bonds) were negative. Since the compound also gave no precipitate with digitonin in alcohol solution, no direct indication can be cited to show that this compound is a phytosterol or phytosteroline.

By boiling several times in dilute hydrochloric acid, the compound is completely decomposed into two components:

a. A reducing sugar which is easily detected in hydrochloric acid solution (Fehling, Luff).

b. An aglucone which forms beautiful glistening hexagonal plates when recrystallized from dilute alcohol (see Figure 2) and is readily soluble in organic solvents.

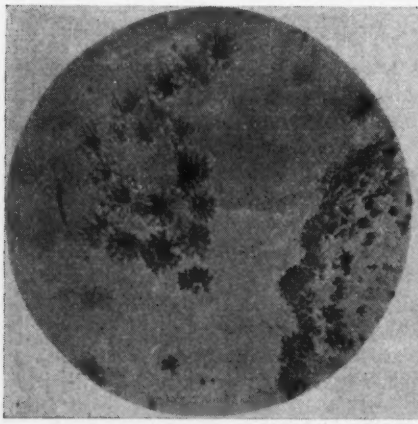


FIG. 1.—Glycoside.

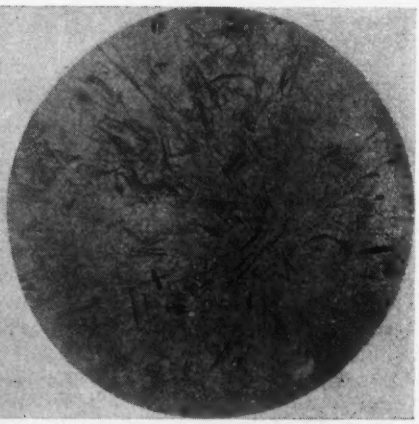


FIG. 2.—Aglucone.

From its melting point and unchanged mixed melting point (131°), the aglucone appears to be identical with the compound described in Section III, 1. The molecular weight is 279, *i.e.*, 176 less than for the glycoside from which it was obtained by hydrolysis. Since this difference approximates the molecular weight of glucose (180), it seemed logical to assume that the sugar component is glucose or at least a hexose. In this connection reference may be made to the steroline obtained by Whitby, Dolid and Yorston[22] ($C_{33}H_{56}O_6$, decomposing at 285-90°, calculated molecular weight 548) and the sterol obtained therefrom by hydrolysis, $C_{27}H_{46}O$, m.p. 134.5, molecular weight 386. In all probability these compounds are identical with the glycoside and aglucone just described. The phytosterol described by Dekker[23], melting at 129°, is probably identical with our aglucone.

As already stated (see Section II, 1), this aglucone gives the color tests of Salkowsky, Liebermann-Burchardt, Mach and Tschugajew. Other tests for phytosterols, however, were negative, and the aglucone, like the glycoside, does not give a precipitate with digitonin.

It may still be noted that Van Dillen[21] confirmed the presence of glucose in latex as early as 1922. Ultee[24], Whitby[25], Belgrave[3], Bruson, Sebrell and Vogt[18], and Bruni[26] have also reported the presence of phytosterols in rubber

latex. The phytosterols separated by Bruson are distinctly different in properties from the aglucone described herein.

V. DISCUSSION

Summarizing the results obtained in previous sections, the crude lipids may be considered as a mixture of lecithins containing glycosides. From the following table, which also contains figures reported by Rhodes and Bishop[6], the significance of the analytical results which have been obtained is at once apparent.

Kind of lecithin	% Composition			Ratio *	Calculated lecithin content (Lg) in whole % according to content of:		
	Liberated fat acids	N	P	N: P	Fat acid	N	P
Stearo-oleo-lecithin (theoretical)†	70.3	1.74	3.85	1: 2.24	100	100	100
Rhodes-Bishop crude product	71.0	0.59	1.72	1: 2.82	101	34	45
Rhodes-Bishop purified product	—	0.88	2.56	1: 2.90	—	51	67
Crude lipids	84.1	0.54	1.58	1: 2.93	120	31	41
Purified lipids	61.3	1.05	2.35	1: 2.24	88	60	61

* We are not entirely clear as to the derivation of the N: P ratios given by Rhodes and Bishop.[6]

† We based our calculation of Lg on stearo-oleo lecithin (molecular weight 805) as a 100% phospholipid. Moreover, it is tacitly assumed (the opposite does not appear in any way from the experiment) that all the observed N occurs as choline and all the P as glycerophosphoric acid in the lecithin molecule.

It is quite noteworthy that wide discrepancies occur in lecithin content (Lg) to the extent that these were calculated from the observed amounts of nitrogen, phosphorus and fat acids. The higher values of Lg were obtained from the fat acid and the lower from the nitrogen content. The latter is comprehensible in view of the ease with which choline splits off (cf. Section III, 1). As for the fat acids, it must be assumed that the purification process (by precipitating lecithins from ether solution with acetone) decreases the fat acid content of lecithins in favor of the nitrogen and phosphorus content. Nevertheless it appears from the Lg values of the purified lipids that these contain relatively too much fat acid. It is entirely possible, indeed probable, that this excess is derived from ordinary fats containing the fat acids combined with glycerol.

Separation of a glycoside is highly important, especially since it is now clear, at least in part, how the sugar component occurs in the highly complicated lipid system, but the manner in which the glycoside is linked to one or more lecithin components is a question which must be left unanswered for the present. The great practical importance of the occurrence of fat acids in plantation latex becomes apparent only as the following considerations receive attention:

According to Rhodes and Bishop[6] the average lipid content of latex may be stated to be 0.2 per cent. These lipids, which contain about 70 per cent free or combined fat acids may thus yield not less than 1.4 grams of fat acids per liter of latex. That this amount of acids is actually liberated is certain in view of the instability of lecithins. This is particularly true of ammoniated latex in which ammonia exerts a catalytic accelerating effect on the ordinary course of lecithin hydrolysis. The same is true of potassium hydroxide and sodium hydroxide, since these bases when added to latex quickly form potassium or sodium soaps in substantial quantity. In view of the important functions of soaps in the latex industry, this circumstance has fundamental practical importance.

VI. SUMMARY

To identify completely the phospholipids, which according to several authors[3, 4, 5, 6] may occur in *Hevea* latex, we separated in a very simple way a butter-like substance, which really contains phospholipids. The results of qualitative analysis justify the positive conclusion that this substance contains lecithins composed of glycerophosphoric acid, choline and the fat acids: palmitic acid, stearic acid, arachidic acid, oleic acid and linoleic acid. A glycoside also was shown to be present in the raw material. We found the content of phosphorus, nitrogen and fat acids to be 1.58, 0.54 and 84.1 per cent, respectively. In purifying the crude material by means of fractional precipitation with acetone from the ether solution, we obtained a nearly colorless gum which contained 2.35 per cent phosphorus, 1.05 per cent nitrogen and 61.3 per cent fat acids. It is stated that the purification is accompanied by a considerable loss of fat acids, the latter remaining in the acetone-ether solution.

REFERENCES

[1] *Chem. Reviews*, **2**, 243 (1925).
[2] "Studien über die Narkose", Jena, **1901.**
[3] *Malayan Agr. J.* **11**, 376 (1923); **13**, 373 (1925).
[4] *Arch. Rubbercultuur* **13**, 384 (1929).
[5] *Arch. Rubbercultuur* **13**, 562 (1929).
[6] *Quart. J. Rubber Res. Inst. Malaya*, **2**, 125, 136 (1930); **4**, 153 (1932).
[7] Wallenstein and Finck, *Chem.-Ztg.* **1894**, 1190.
[8] Van Harpen, *Arch. Rubbercultuur* **21**, 113 (1937).
[9] *Boll. chim. farm.* **50**, 309 (1911).
[10] *Apoth. Ztg.* **26**, 912 (1911).
[11] Paal, *Biochem. Z.* **211**, 244 (1929); E. H. and A. Winterstein in Klein's "Handbuch der Pflanzen-Analyse", II, 700, Vienna, **1932.**
[12] *Bull. Soc. Chim.* [4] **11**, 805 (1912).
[13] "Deutsche Einheits-Methoden", **1930**, 54.
[14] Cf. among others Van Leent, "Analyse en Warenkennis der voornaamste vette lichamen", Amsterdam, **1934.**
[15] *Rec. trav. chim.* **58**, 281 (1939).
[16] Schoorl, "Organische analyse II", Amsterdam **1937**, 275.
[17] Kobel and Neuberg in Klein's "Handbuch der Pflanzen-analyse" II. 546, Vienna, **1932.**
[18] For occurrence of higher fatty acids in rubber see, among others, Whitby, *J. Soc. Chem. Ind.* **42**, 336T (1923); Dekker, *India-Rubber J.* **70**, 815 (1925); Van Rossem and Dekker, *Ind. Eng. Chem.* **18**, 1152 (1926); Bruson, Sebrell and Vogt, *Ind. Eng. Chem.* **19**, 1187 (1927).
[19] Kraay and Altman, *Arch. Rubbercultuur* **22**, 223 (1938).
[20] On this point see, among others, Czapek, "Biochemie der Pflanzen", Jena, **1913**, I. 786; Sobotka, "Chemistry of the Sterids", Baltimore **1938**; Fieser, "The Chemistry of natural products related to phenanthrene", New York, **1936**, 117; Dalmer in Klein's "Handbuch der Pflanzenanalyse" II, 712, Vienna, **1932.**
[21] *Arch. Rubbercultuur* **6**, 263 (1922).
[22] *J. Chem. Soc.*, **1926**, 1453.
[23] *India-Rubber J.*, **70**, 816 (1925).
[24] *Chem. Weekblad* **9**, 773 (1912).
[25] *Ann. Rep. Brit. Assoc. Adv. Science* **59**, 432 (1923), *Science* **54**, 174 (1921).
[26] *Giorn. Chim. Ind. Appl.*, **9**, 161 (1927).

A CONTRIBUTION TO KNOWLEDGE OF THE CREAMING PROCESS *

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I. INTRODUCTION

Creaming of latex is a process which is extensively employed, partly because good creaming agents have been developed[1] and partly because of the constantly increasing demand for concentrated latex.

Knowledge of the mechanism of creaming is not in proportion to the great practical importance of the process. It still happens too frequently that unexpected variables or phenomena, for which the laboratory investigator can offer no explanation, are encountered.

In the present paper we present the preliminary results of tests carried out at the West Java Experiment Station. For a general survey of creaming processes, reference should be made to a recent paper by Kraay[2].

The object of the present paper is to enquire more deeply into various phenomena which are discussed briefly in the paper cited above.

Unless otherwise stated, the tests to be described were made with konjak flour, abbreviated here to K flour.

II. FORMATION OF AGGLOMERATES

The essential feature in the mechanism of creaming is agglomeration.

It has already been demonstrated by Baker[3] that when a creaming agent is added the separate latex particles cohere in clusters.

As a result of this agglomeration, kinetic thermal motion ceases to have much influence on individual particles, and the difference in specific gravity causes the clusters to rise.

The ascending clusters collect at the top of the liquid to form a cream, which continues to become thicker, while the lower liquid layer from which rubber is being constantly withdrawn becomes clearer.

The phenomenon described here can be observed easily in creaming a very dilute latex and in the formation of cream on milk. With latex, however, containing 5-10 or more per cent of rubber, entirely different phenomena are observed.

Some time after adding the creaming agent, a cream layer of serum may be seen separating at the bottom of the liquid. Separation from the supernatant liquid is indistinct at first, but soon becomes sharper, with a tendency to move upward, *i.e.*, the volume of serum increases while the volume of cream decreases. After about two days, the volumes become practically constant. In this last case the concentration of rubber globules is apparently so great that the agglomerates unite to form a mass extending throughout the liquid.

For a clear understanding of the following discussion, we wish to emphasize also that the phenomena described here are purely mechanical. When the ag-

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glomerates have once been formed, creaming can be greatly accelerated, *e.g.*, by replacing the gravitational field with a field of enormously stronger centrifugal force.

III. MECHANISM OF AGGLOMERATION

A. Microscopic Observation

The union between rubber globules in an agglomerate is completely reversible. When the agglomerate is introduced into water, the individual rubber particles are liberated again. Under the microscope this disintegration of agglomerates can be very clearly observed in the following manner:

Place on an object glass, about 0.6 cm. apart, a drop of freshly prepared cream and a drop of water. Lay a cover glass cautiously over both drops in such a way

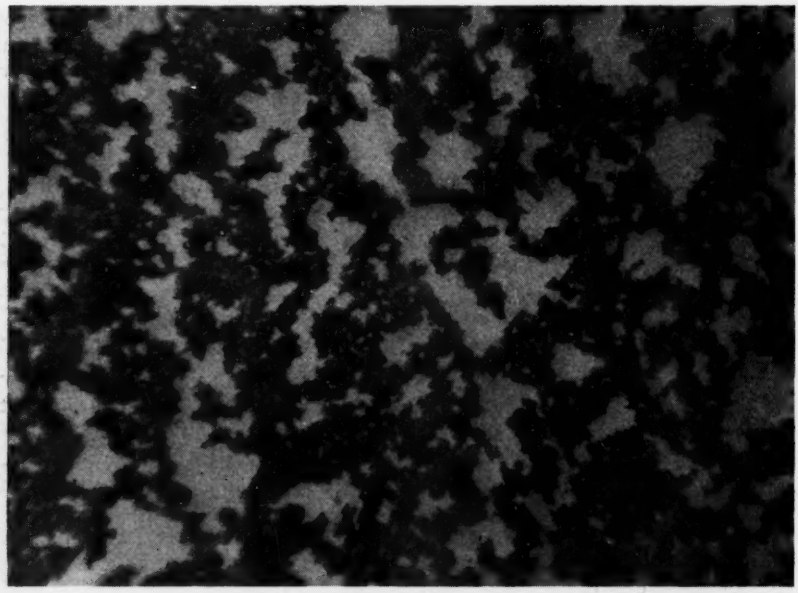

Fig. 1.—Cluster formation, photographed by transmitted light.

that a sharp line is formed between cream and water. If the microscope is focused exactly on this boundary line, the following may be observed:

More or less large clusters detach themselves, and these clusters diffuse into the water. The clusters themselves very quickly disintegrate into smaller agglomerates and individual rubber particles showing a lively Brownian movement.

Now it was very quickly apparent to us that in some cases disintegration took effect much more rapidly than in others, especially when the cream was fresh, *i.e.*, when the latex: K flour mixture had stood only a few hours disintegration was faster than when the mixture had stood one or several days.

If a drop of latex is investigated in the same manner shortly after mixing with the K flour solution, it even gives the impression of having no agglomerates present at all, since only individual particles diffuse into the water phase from the cream layer. Moreover the cream: water interface becomes indistinct much more rapidly than when the cream is old.

Microscopic examination of undiluted latex already mixed with K flour and pressed to a very thin layer between two slides indicates, however, that agglomerates must be formed immediately after mixing. Moreover this is confirmed by the observations described below.

For the sake of completeness we may say also that agglomeration can often be observed with the unaided eye or under a lens when a latex: K flour mixture is stirred in a beaker and liquid draining from the wall is examined.

B. Experiments with Centrifuge Tubes

As mentioned already, creaming can be greatly accelerated by using a centrifuge. For this purpose part of the latex: K flour mixture is centrifuged 15 to 20

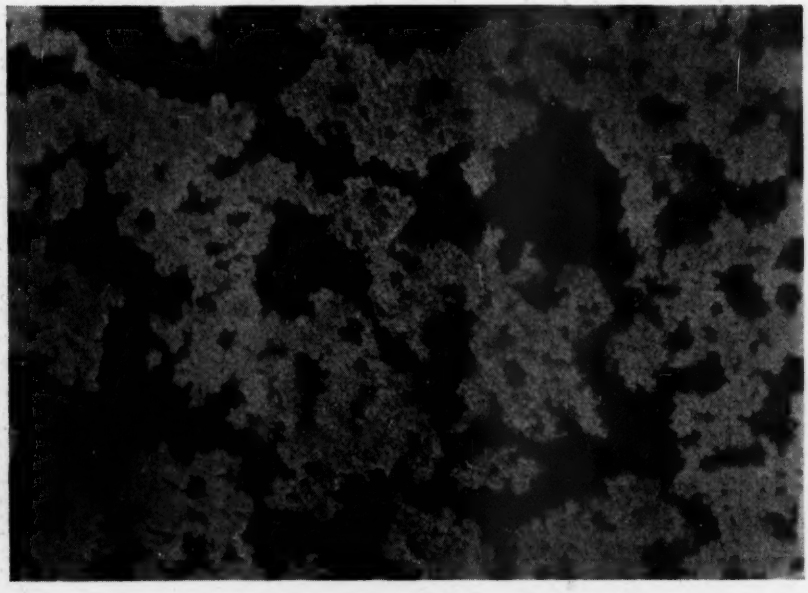

Fig. 2.—Cluster formation, photographed in dark-field illumination.

minutes in a calibrated centrifuge tube. A very sharply defined cream layer separates, which shows practically no increase in volume if centrifuged longer.

If, however, the tube is allowed to stand for a day and centrifuged again, it appears that cream volume is progressively decreasing by a substantial amount.

The tests can also be made in another way. A freshly prepared latex: K flour mixture is divided in 3 calibrated centrifuge tubes. Tube *A* is centrifuged directly and the volume of cream is observed. Tubes *B* and *C* are allowed to stand at rest. After 1-4 hours, tube *B* is centrifuged and the next day tube *C*. It then appears that *C* has the smallest volume of cream and *A* the largest. Since the serum is equally clear in all three tubes, it may be concluded that the rubber particles are most closely packed in tube *C*, while packing is much looser in tube *A* immediately after centrifuging.

C. Explanation of Syneresis in Cream

Observations of tubes *A* and *B* demonstrate that immediately after mixing latex with a creaming agent, the rubber particles in agglomerates are loosely packed and occupy a large volume. After a time union becomes firmer, agglomerates are more difficult to separate, and they occupy a smaller volume. This phenomenon of attraction in agglomerates with simultaneous separation of serum is designated "cream syneresis" by analogy with the familiar syneresis

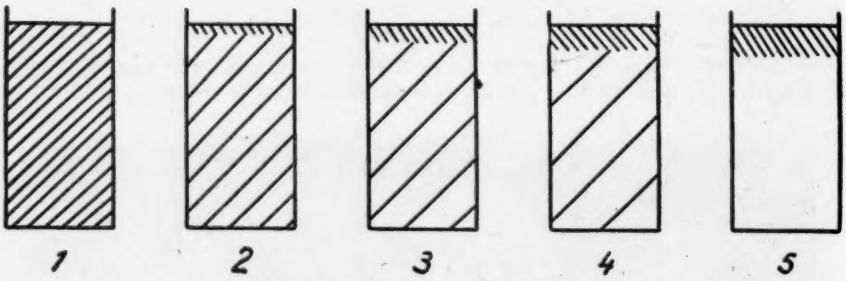

Fig. 3.—Creaming of extremely dilute latex.

phenomenon in colloid chemistry[4]. Quite independently of us Twiss and Carpenter, from exact motion analysis at the cream:serum interface, also advanced the hypothesis that creaming proceeds in two phases which they call "cluster migration" and "network shrinkage".

The general explanation of syneresis can also be applied to cream. It is known that rubber particles in latex have a negative charge by reason of proteins adsorbed on the surface. Without this charge the particles would immediately

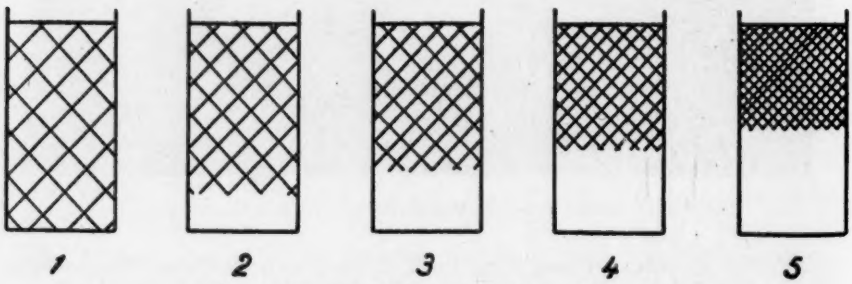

Fig. 4.—Creaming of latex of normal concentration.

unite (flocculate) on impact, since there are also forces of attraction at the particle surface. These forces of attraction are of two kinds, first the socalled van der Waals forces and, second, such forces as may result from positive charges derived from induced and perhaps also from permanent dipoles present in protein molecules. The resultant of the forces of repulsion and attraction governs the particle behavior.

Now the negative charge is not uniformly distributed over a colloidal particle surface but is present as a discontinuum. In all probability the van der Waals forces, being inherent in the substance (in this case rubber), are distributed over the surface as a continuum. Thus there are points on a rubber globule where

repulsion is very strong. At certain points it is weaker, and it is even possible that points may occur where attraction predominates.

It may be assumed that in freshly formed agglomerates individual particles still retain part of their kinetic mobility.

Whereas after adding the creaming agent, particles in a cluster are oriented quite arbitrarily with respect to each other, in the course of time they take up positions with points of minimum repulsion force turned toward each other, thus permitting closer approach. The particles rotate just long enough to seek out the lowest energy positions. This is coupled with compact structure, increase in mutual combining forces, and expulsion of serum.

IV. THEORIES OF AGGLOMERATION

A. The Theory of Vester [5]

Vester assumes that creaming agents react with proteins in the serum to form a simple coacervate. Such coacervates have indeed been observed on mixing, for example, agar with casein, and are considered to result from mutual desolvation of colloids (this cannot be a case of a complex coacervate, since both creaming agent and rubber are negatively charged).

Vester reports that he observed coacervation in the serum layer on adding a creaming agent and after centrifuging. We repeated the tests with fresh latex, but were unable to observe the phenomenon which he describes. We used the following creaming agents: K flour, gum tragacanth, karaya gum and sodium polyvinyl acrylate. Approximately 1 per cent solutions of these substances were prepared, and different amounts of solution were mixed with different amounts of latex serum. The serum was obtained by centrifuging fresh ammoniated latex in a modern de Laval separator (laboratory machine type L6), with suitable adjustment and such small capacity that a serum with extremely low rubber content was obtained. This serum was then centrifuged a second time. By this means the dry rubber content (DRC) was lowered to about 0.5 per cent.

Under the microscope no rubber globules could be observed with ordinary illumination in this serum; they could be detected only by ultramicroscopic examination with a cardioid condenser.

On adding a creaming agent, it was observed that at suitable concentrations these ultramicroscopic particles joined to form agglomerates which were visible in the microscope. We never observed emulsification such as Vester described.

Another test series was carried out with serum obtained from a low rubber sublatex fraction (centrifuged once) by filtering through Chamberlain filter candles. The resulting serum was perfectly clear, and still had a high protein content.

Solutions with creaming agents were freed from coarse particles by centrifuging in a centrifuge tube and decanting. These solutions also were perfectly clear.

Varying amounts of serum and creaming agent were then mixed together, but in every case the solutions remained clear.

Absence of emulsification, however, is not sufficient proof that coacervation did not occur, yet there are other facts which contradict the theory proposed by Vester:

1. During creaming, serum proteins are not entrained by the rubber globules. Otherwise it would be impossible to make low-protein rubber by repeated creaming.

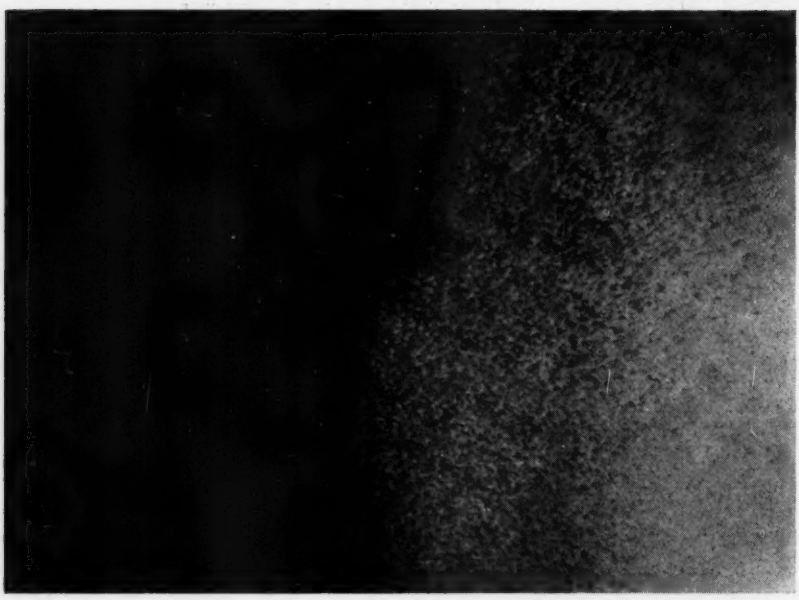

FIG. 5A.—Fresh cream.

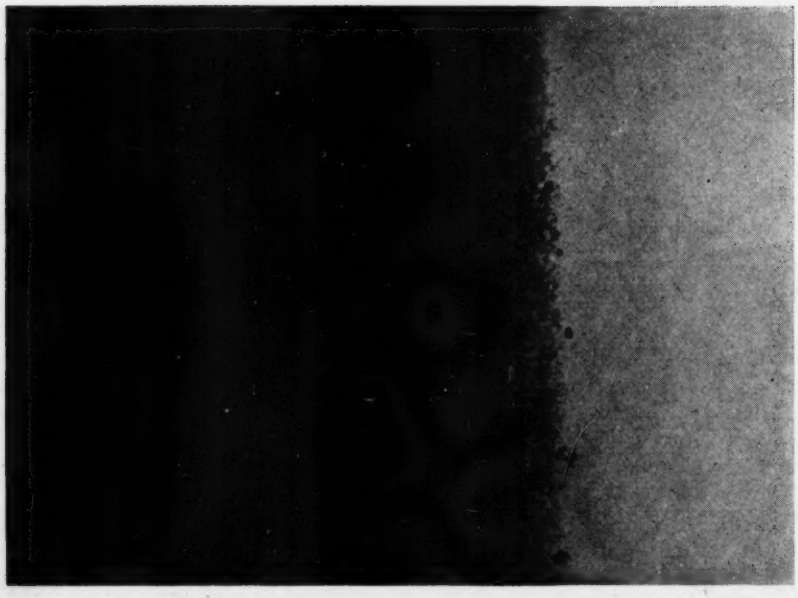

FIG. 5B.—Redisintegration of clusters. Magnification 200× (transmitted light).

2. Even latex with very low protein content can be creamed.
3. Paraffin emulsions prepared with any desired emulsifier (protein-free) can also be creamed (see Section V).

Hence proteins do not have any essential part in creaming. Their sole function is to impart a certain charge to rubber particles. This function can be performed equally well by other emulsifiers.

B. Theory of Twiss and Carpenter [6]

This theory is based on McBain's hypothesis[7] that high viscosity in hydrophilic colloids, including creaming agents, is caused by a tendency of the particles to unite in a network within which the solvent (water) is firmly held. This network, however, behaves toward deformation as would be expected in the case of stirring or flow through a tube.

When a solution of a hydrophilic colloid is added to latex, the rubber particles join with molecules of the added colloid by adsorption at the interface. If it is considered that particles of the added hydrophilic colloid are already cohesively joined, we have an explanation for the occurrence of rubber particles in agglomerates.

A network of creaming agent molecules is then present between which the rubber particles are held (anchoring effect). Indeed many phenomena can be explained by this hypothesis. More exact investigation is needed, however, first with respect to the validity of McBain's hypothesis and, second, with respect to the reason why the negative creaming agent is adsorbed by rubber particles, also negatively charged.

C. The Creaming Process

A counterpart of creaming is the reversible flocculation of coal suspensions by hydrophilic colloids, as is done in many coal mines.

The waste water, which is rich in coal particles, is treated with a specially prepared starch, which causes the coal particles to agglomerate and sink. It has been found recently that K flour is also an excellent flocculating agent for this purpose[8].

Theories concerning this phenomenon have been suggested by several investigators[9]. In our opinion it has the same fundamental mechanism as creaming. In connection with the following discussion, we wish to direct attention to the fact that when a coal slurry is flocculated with electrolytes, the fraction which sinks occupies a much larger volume than when colloids are employed. The first method of flocculation involves a decrease in electric charge, whereas in the second method there is little or no such decrease.

V. INFLUENCE OF THE CONCENTRATION OF CREAMING AGENT ON THE DRY RUBBER CONTENT OF CREAM AND SERUM

Previous investigations have already studied the influence of the concentration of creaming agent so that a brief statement will suffice here.

With increasing quantities of creaming agent, the lower serum layer becomes progressively clearer. At the same time, however, cream volume increases. Determination of the DRC content of the cream usually reveals an initial rise followed by a progressive decrease. Thus there is always an optimum concentration at which creaming is most efficient.

The fact that the same phenomenon is observed in creaming a paraffin emulsion with K-flour shows that the effect is not limited to latex.

The paraffin emulsion is prepared as follows:

Solution A:	
Liquid paraffin	88 parts by weight
Stearic acid	9 parts by weight
Solution B:	
Water	300 parts by weight
Triethanolamine	3.5 parts by weight

Solutions A and B are poured together into a Charlotte colloid mill. An emulsion is formed with active frothing, and is passed through the machine several times, then allowed to stand overnight to give the air bubbles time to rise.

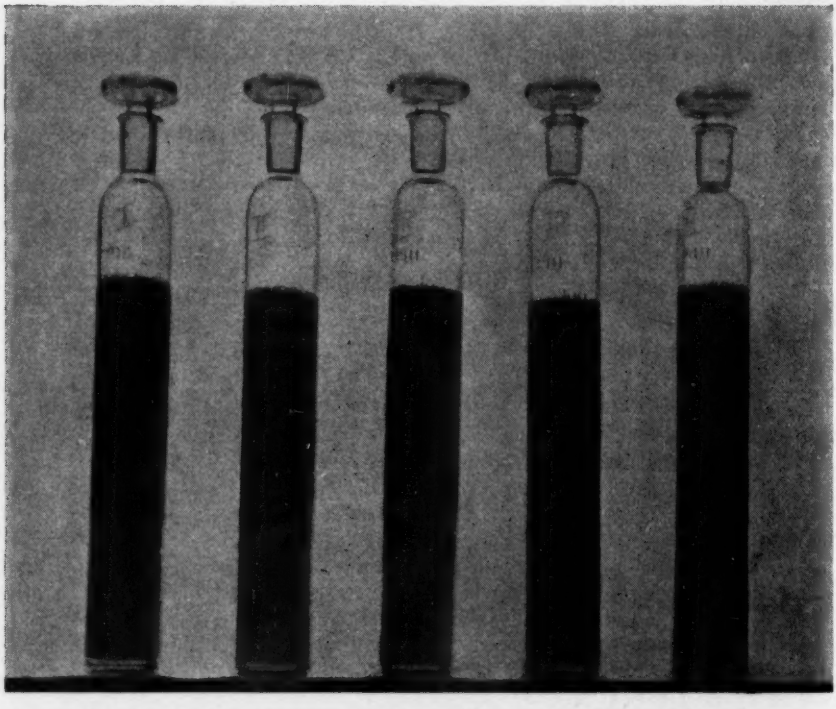

FIG. 6.—Creaming of a paraffin emulsion with increasing proportions of K flour.

Although the emulsion was very stable, it showed some slight creaming on standing. In contrast to the usual appearance in natural creaming (without creaming agents) the interface between clear serum and cream was quite sharp. This agrees with the fact that agglomerates were visible in the undiluted emulsion even without creaming agents. When the emulsion was diluted about ten times with water, the agglomerates disappeared, and natural creaming no longer gave a sharp cream:serum interface.

Under the influence of only a little creaming agent, such as K flour, creaming immediately became much more nearly complete. The series illustrated in Figure 6 was prepared with 5, 8, 10, 13, 16 and 20 cc., respectively, of 1 per cent K flour solution per 100 cc. of mixture.

For most latexes, the optimum K flour concentration is 14 cc. of 1 per cent solution per 100 cc. of latex. This optimum, however, depends to some extent on the electrolyte content in the serum and rubber content in the latex. Although this point is to be investigated more in detail, we quote the following figures here by way of illustration:

In a given case, for example, the optimum concentration for dialyzed latex was 25 per cent of 1 per cent K flour solution; after adding 3 millimols of potassium thiocyanate per 100 cc. of latex, the optimum was 20 per cent, and with 5 millimols of potassium thiocyanate per 100 liters (error for cc.?—JFS) of latex it was 17 per cent.

The influence of the DRC content of latex is illustrated by the following figures.

Latex	DRC (%)	Optimum K flour concentration (%)
A	47.5	6
B	30.3	14
C	24.8	27

Latex B was ordinary ammoniated plantation latex. One portion of this latex was centrifuged in a milk separator.

Latex A was a mixture of latex B with centrifuge cream.

Latex C was a mixture of latex B with centrifuge serum.

Thus there were three latexes with different concentrations of rubber but with identical concentrations of serum (of course the average particle size varied somewhat).

Figure 7 illustrates more clearly the influence of the K flour concentration in these three latexes.

VI. INFLUENCE OF ELECTROLYTES ON THE DRY RUBBER CONTENT OF CREAM AND SERUM

The influence of electrolytes on creaming has already been investigated at the West Java Experiment Station by G. M. Kraay (not published). The effect was especially conspicuous in latex which had been partially freed from serum components by repeated creaming.

The influence of electrolytes or of serum components in general on creaming appears immediately in repeated creaming of latex. That is, every time the serum is drawn off a portion of the protein is removed. When the resulting cream is diluted with distilled water and creamed again, creaming is much less thorough, and by the third or fourth time no creaming can be observed at all. As will be discussed in the next section, this results from the pH value being too low by reason of insufficient ammonia concentration. For this reason aqueous ammonia should always be used for dilution in repeated creaming to maintain the needed ammonia content. But even when this precaution is taken, each successive creaming will be slower and less complete than the preceding one, chiefly because proteins and salts are being removed.

For a systematic study of the influence of serum components on creaming, it would be well to start with latex from which serum components have been extracted as thoroughly as possible, so that the isolated components can be returned to the latex in varying quantities and their effects on creaming can be observed.

For the present we shall limit ourselves to the influence of electrolytes.

In the tests described here, the concentration of creaming agent was always kept constant. For low protein latexes, 25 cc. of 1 per cent K flour solution was used per 100 cc. of mixture. For dialyzed latexes not in the low protein class, this quantity was changed to 200 cc. In every case the K flour suspension was freed from coarse particles by filtering through a cloth, so that these particles would not interfere in determining serum and cream volume.

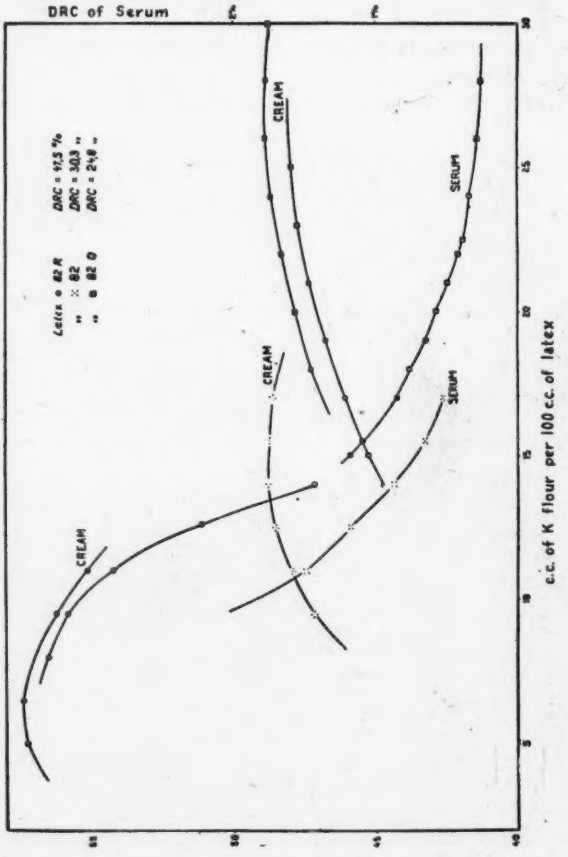

FIG. 7.—DRG cream and serum as a function of the K flour concentration. (For latices of different concentrations.)

A. TESTS WITH LOW PROTEIN LATEX

Ordinary plantation latex (2.5 liters) was creamed five times successively. The cream obtained after the fifth creaming was diluted with ammoniated water to a DRC content of 19.5 per cent, while the ammonia content was 26.05 milli-equivalents per liter.

A series of tests was carried out with increasing concentrations of potassium chloride, potassium iodide, potassium thiocyanate, calcium chloride and barium chloride, but with the same rubber content. The separate series were always started at the same time. K flour was added only after the entire series had been provided with the specified quantity of electrolyte.

After two days, when the volume of cream did not undergo much further change, the cream and serum were drawn off separately and the DRC content was determined. This determination offered no difficulties in low protein serum. The results are shown in Table I.

To repeat this test on a more extensive scale, four liters of latex were repeatedly creamed. To make sure that all electrolytes were removed, creaming was preceded by dialysis for 24 hours with ordinary tap water. Creaming was carried out four times.

TABLE I

INFLUENCE OF ELECTROLYTES ON LATEX CREAMED 5 TIMES

Electrolyte	Concentration millimols per 100 cc.	DRC content	
		Cream	Serum
KCl	0	47.6	0.46
	2	49.1	0.14
	4	48.3	0.10
	7	46.3	0.08
	10	45.3	0.02
	15	38.3	?
KI	2	50.7	0.22
	4	50.2	0.18
	7	49.0	0.12
	10	47.0	0.06
	15	36.9	?
KCNS	2	48.8	0.10
	4	47.1	0.06
	7	45.3	0.04
	10	50.2	0.08
$CaCl_2$	0.018	49.6	0.36
	0.036	49.9	0.36
	0.072	49.7	0.28
	0.144	45.5	0.22
	0.216	43.1	—
$BaCl_2$	0	47.6	0.58
	0.025	48.2	0.56
	0.05	46.5	0.50
	0.10	42.4	0.34
	0.2	19.5	0.20
	0.3	18.3	?

The DRC content after diluting the cream was 17.7 per cent; the ammonia content 269.5 milliequivalents per liter; the nitrogen content 0.22 per cent of the total solids.

The following series were prepared in this way:

1. Addition of KCl, NaCl, LiCl and NH_4Cl.
2. Addition of KCl, $CaCl_2$, $AlCl_3$.
3. Addition of $CaCl_2$, $BaCl_2$, $SrCl_2$.
4. Addition of KCl, KBr, KI, and KSCN.

Since the volume of cream changed very little after two days, it may be said that the observed DRC content gives a good idea of the final state in the creaming process.

TABLE II

SUMMARY OF RESULTS OBTAINED WITH DIALYZED LOW PROTEIN LATEX

(Mixture: latex 65 cc., 1 per cent K flour 25 cc., electrolyte solution 10 cc.)

Electrolyte	Concentration, millimols per 100 parts	DRC content	
		Cream	Serum
KCl	0	44.2	0.26
	2	42.8	0.08
	4	40.7	0.06
	8	35.0	0.04
	12	33.8	0.02
	16	32.6	0.02
$CaCl_2$	0	44.2	0.26
	0.018	44.1	0.20
	0.036	43.4	0.26
	0.072	41.8	0.22
	0.144	37.6	0.12
	0.216	28.2	0.08
$AlCl_3$	0	44.5	0.28
	0.025	43.8	0.28
	0.05	43.5	0.26
	0.1	42.6	0.20
	0.2	39.9	0.12
	0.4	33.2	0.04
$CaCl_2$	0	41.0	0.14
	0.018	40.7	0.10
	0.036	39.5	0.08
	0.072	38.2	0.10
	0.144	33.2	0.04
	0.216	30.5	—
$SrCl_2$	0	45.7	0.30
	0.025	46.0	0.30
	0.05	45.4	0.26
	0.1	44.4	0.24
	0.2	37.5	0.12
	0.3	29.4	0.06
$BaCl_2$	0	45.7	0.30
	0.025	45.0	0.26
	0.05	44.5	0.24
	0.1	41.8	0.16
	0.2	32.3	0.10
	0.3	26.4	0.07

Electrolyte	Concentration, millimols per 100 parts	DRC content	
		Cream	Serum
KCl	0	48.2	0.46
	2	48.4	0.14
	4	45.0	0.06
	8	40.6	0.04
	12	37.0	0.08
	16	35.6	0.04
NaCl	0	48.2	0.46
	2	47.7	0.10
	4	44.0	0.04
	8	36.2	0.02
	12	36.7	0.04
	16	33.5	0.04
LiCl	0	48.2	0.46
	2	45.5	0.06
	4	40.9	0.06
	8	35.9	0.02
	12	31.8	?
	16	28.7	?
KBr	0	42.1	not
	2	41.7	deter-
	4	40.6	mined
	8	37.4	
	12	34.7	
	16	35.0	
KCl	0	42.1	
	2	41.6	
	4	40.5	
	8	37.5	
	12	35.0	
KSCN	0	42.1	
	2	42.4	
	4	39.0	
	6	36.8	
	8	36.5	
	10	33.9	
	13	35.0	
KI	0	42.1	
	2	41.4	
	4	34.8	
	7	38.6	
	10	36.8	
	13	36.4	

The following conclusions may be drawn from the experiments described above:

A. EFFECTS ON CREAM

1. Electrolytes have in general the property of decreasing the DRC content of the cream.
2. In some cases at low concentration they may increase the DRC content.
3. Divalent ions are effective at much lower concentrations than monovalent ions. Trivalent ions are no more potent than divalent ions.
4. The descending order of activity for monovalent ions is: Li, Na, K.
5. For divalent ions the order of activity is: Ba=Ca>Sr.
6. The influence of anions cannot be arranged in a definite sequence.

B. EFFECTS ON SERUM

1. Addition of electrolytes gives a clearer serum (see Figures 8 and 9).

2. Again with respect to effect on the DRC content of serum, divalent ions are effective at much lower concentrations than monovalent ions, although the influence is less pronounced than in the cream.

3. With respect to the rate of creaming, the following statement may be made: Creaming is always preceded by the formation of characteristic irregular interstices filled with serum. It is evident that creaming begins suddenly here and there without affecting the remainder of the liquid. This phenomenon appears first in the vials with the lowest electrolyte concentrations. Homogeneity is retained longest at the highest electrolyte concentrations. If so much electrolyte is added that the latex begins to coagulate, no creaming occurs at

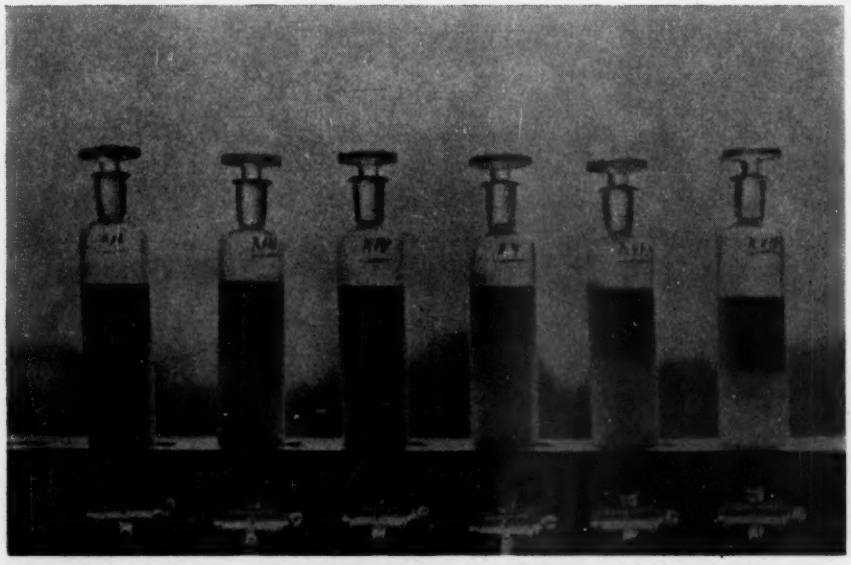

FIG. 8.—Creaming of dialyzed latex of low protein content with increasing amounts of $BaCl_2$; photograph taken after 48 hours.

all. These phenomena are followed by the formation of cream:serum interfaces. At first this interface is indistinct, but it becomes sharper as its level rises. Movement of the interface is very irregular in the various samples, especially at the beginning.

In most series, however, we were able to observe that the interface rose fastest at a definite electrolyte concentration, and that creaming was slowest at lower or higher concentrations. From this we concluded that the phenomenon of Conclusion A, 2, above is general, but can be distinctly observed only in exceptional cases.

The various cream volumes resulting from various electrolyte concentrations are best observed after 1 to 10 hours.

In time the differences become smaller. After 48 hours cream volume undergoes very little change, although differences are still distinctly discernible (see Figure 8).

B. Tests with Dialized Latex of Normal Protein Content

We always used fresh ammoniated plantation latex, which was dialyzed at least 24 hours immediately after being received in the laboratory. Ordinary tap water was used for rinsing. About 1 to 12 hours after dialysis began, the concentration of ammonia had fallen so low that it was necessary to add more ammonia.

After dialysis was completed, ammonia was again added to bring the final concentration to about 5 grams per liter.

Creaming tests showed precisely the same phenomena as with dialyzed low-protein latex. In every instance the observed differences were quantitative, not qualitative.

The most conspicuous feature was the wide variability among various latex samples. Although the origin of the latex was always noted, no simple relation was observed. The situation was complicated still further by the fact that the tests coincided with the beginning of the shedding season. In general it may be said that the influence of electrolytes in this case is less than with low protein latex or, in other words, higher electrolyte concentration is necessary to produce the same effect.

It may be seen in Table III, for example, that the electrolyte effect was extraordinarily small in latex 66 A; in fact so small that, even at a concentration of 16 millimols per 100 cc., there was no decrease in the DRC content of the cream.

In contrast to Table II, it is evident in almost every case that at low electrolyte concentrations the DRC content of the cream first increases, then decreases at higher concentrations.

It may also be mentioned that the presence of protein makes it difficult to determine the DRC content of serum. It was found necessary to hydrolyze these proteins before rubber in the serum could be coagulated with acid[10].

In general it appeared that in creaming latex containing proteins the serum contains more rubber than in creaming low-protein latex.

C. Paraffin Emulsions

To ascertain whether an electrolyte has any influence in this type of creaming too, the following test was made. To 90 cc. of emulsion there were added 5 cc. of 1% K flour solution and 5 cc. of potassium chloride solution at different concentrations such that the concentration of potassium chloride per 100 cc. of mixture was 0, 0.2, 0.4, 0.8, and 1.0 millimol. The results after 2 days are shown in Figure 9.

These simple tests suffice to prove that, aside from specific differences, creaming of entirely arbitrary emulsions proceeds in exactly the same way as the creaming of latex.

VII. INFLUENCE OF THE pH VALUE ON THE DRY RUBBER CONTENT OF CREAM AND SERUM

Whereas in the preceding tests care was always taken to keep the pH value constant throughout the series by using neutral salts as electrolytes, special attention is devoted to the pH value in this section.

From preliminary tests, the following conclusions had already been derived:

1. The concentration of ammonia has no influence on creaming within wide limits unless it is allowed to fall below a certain level, at which creaming is much less effective.

TABLE III

INFLUENCE OF ELECTROLYTES ON CREAMING OF DIALYZED LATEX

(Mixture: latex 70 cc., 1 per cent K flour 20 cc., electrolyte solution 10 cc.)

Electrolyte	Concentration, millimols per 100 parts	DRC Cream	DRC Serum
Latex No. 64A DRC 25.0 per cent			
KCl	0	46.3	0.84
	2	43.6	0.52
	4	39.6	0.38
	8	31.5	0.20
	12	27.1	0.13
	16	23.3	—
$BaCl_2$	0	46.3	0.84
	0.025	46.3	0.76
	0.05	46.0	0.78
	0.1	45.2	0.72
	0.2	42.2	0.52
	0.3	37.8	0.45
$AlCl_3$	0	46.1	0.82
	0.025	46.9	0.64
	0.05	46.6	0.62
	0.1	46.4	0.58
	0.2	45.5	0.52
	0.4	38.2	0.34
	0.6	33.6	0.23
Latex No. 71A			
$CaCl_2$	0	49.9	0.92
	0.2	50.6	0.76
	0.5	48.2	0.52
	0.7	46.2	—
	1.0	coag.	—
$SrCl_2$	0	49.9	0.92
	0.1	50.0	0.86
	0.35	49.9	0.70
	0.5	46.2	0.56
	0.65	39.2	0.38
$BaCl_2$	0	48.9	0.84
	0.25	48.2	0.60
	0.35	42.5	0.22
	0.5	almost no creaming	
	0.65	no coag.	

Electrolyte	Concentration, millimols per 100 parts	DRC Cream	DRC Serum
Latex No. 66A DRC 28.4 per cent			
KCl	0	44.2	0.98
	2	45.2	0.60
	4	45.8	0.60
	8	45.4	0.44
	12	45.2	0.46
	16	44.9	0.46
NaCl	0	44.2	0.98
	2	45.3	0.56
	4	45.8	0.44
	8	45.9	0.48
	12	45.7	0.42
	16	45.3	0.42
LiCl	0	44.2	0.88
	2	45.4	0.56
	4	45.7	0.46
	8	45.3	0.34
	12	44.7	0.3
	16	44.5	0.30
Latex No. 72A			
KCl	0	41.6	0.88
	6	43.3	0.54
	12	42.3	0.50
	20	40.7	0.48
	30	38.8	0.42
	40	37.1	0.42
NaCl	0	41.6	0.88
	12	42.2	0.48
	20	40.0	0.44
	30	37.9	0.40
	40	34.0	0.36
LiCl	0	40.8	0.74
	6	32.9	0.46
	12	41.1	0.42
	20	38.7	0.42
	30	32.9	0.34
	40	18.5	—

This lower limit is, however, somewhat above the minimum quantity required to keep latex in good condition for 2 or 3 days.

2. The addition of small amounts of sodium hydroxide or of potassium hydroxide sometimes gives a richer cream.

Tests: Normal plantation latex ammoniated with 20 cc. of 18 per cent aqueous ammonia was diluted to twice its volume with distilled water and creamed without adding ammonia or potassium hydroxide.

Now the ideal procedure would be to carry out a series of cream tests in which all other factors remain constant while the pH value is varied. Unfortunately this is impossible. It must be remembered that as the pH value changes, the salt concentration also changes. The change in pH with changing content of am-

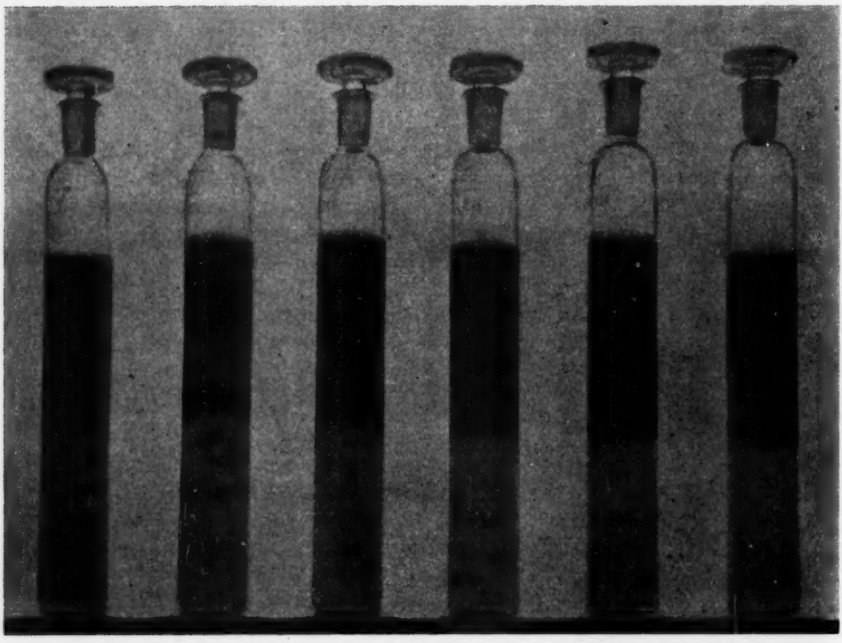

FIG. 9.—Influence of the electrolyte concentration on the creaming of a paraffin emulsion.

monium hydroxide or sodium hydroxide depends on the buffer capacity of the latex sample. This is illustrated by the data in Tables VI and VII (the pH determinations were made with a Leeds-Northrup glass electrode calibrated with borate:NaOH buffers as described by Sörensen, while the pH value was also measured against the H electrode as a control).

TABLE IV

No.	Extra 18% NH_4OH per 100 cc. of mixture	10% KOH per 100 cc. of mixture	DRC (Cream)
1	0	0	25.61
2	1½	0	44.96
3	1½	1	47.54
4	1½	3	31.56

From this it may be seen that: (1) Normal latex has a much greater buffer effect than dialyzed latex; (2) within very wide limits the pH value changes but little with change in the concentration of ammonium hydroxide; (3) in ordinary latex the pH value cannot be raised above 10.4, and in dialyzed latex above 11.0 by adding ammonia. These limits can be exceeded only with sodium hydroxide.

For dialyzed low-protein latex, the titration values lie between those for pure water and dialyzed latex.

Next we made tests with varying ammonium hydroxide and sodium hydroxide content, while measuring the pH value of the mixture. The results are shown in Table V.

It may be seen that the maximum creaming occurs between pH values 10.8 and 11.8, and that the DRC content of serum is also highest in this pH range, decreasing at lower or higher pH levels.

In the ammonia series, the maximum creaming occurs in the pH range 9.6 to 10.2. It is evident that the values in the sodium hydroxide series are entirely different. This is because of the great difference in cation concentration.

The values in the ammonia series nearly coincide with those for dialyzed latex.

TABLE V

INFLUENCE OF THE pH VALUE ON CREAMING. A. DIALYZED LOW-PROTEIN LATEX (INITIALLY CONTAINING AMMONIA)

Added substance	Milliequiv. per 100 cc.	pH	DRC	
			Cream	Serum
Formic acid	0.8	9.4	27.5	not determined
	0.4	9.8	36.2	0.04
	0.2	10.2	41.8	0.10
	0	10.9	43.9	0.24
NaOH	0.5	11.2	44.3	0.20
	1.0	11.9	43.5	0.20
	5	12.9	29.3	—
	10	13.1	27.0	0.025

TABLE VI

INFLUENCE OF pH ON CREAMING. B. DIALYZED LATEX (INITIALLY NH_3-FREE)

Amount of NH_3 milliequiv. per 100 cc.	pH	DRC	
		Cream	Serum
3	9.34	39.4	0.54
6	9.71	48.6	0.76
12	10.08	49.1	0.82
18	10.22	48.4	0.84
30	10.56	40.4	0.74
42	10.65	31.5	0.48
60	10.67	31.4	0.45

Amount NaOH	Amount NH_3			
2	6	10.86	42.27	0.74
4	6	12.26	Scarcely any creaming	
6	6	12.66	No creaming	
8	6	12.72	No creaming	

VIII. DISCUSSION OF RESULTS

On surveying the results of the above experiments, it is evident that the basis of all these phenomena must be sought in the electric charge on the rubber particles. Indeed it is known[11] that the addition of electrolytes decreases the charge on the rubber particles. The same is true when the pH value of the medium is changed[11, 12]. On adding sodium hydroxide the charge increases, passes through a maximum and decreases again. Electrolyte influence is a very general phenomenon in colloid chemistry, while the influence of the pH value on the charge is characteristic of proteins and phosphatides, among others.

The most striking feature of the data in Tables I and II is the close resemblance to electrophoresis data (for example, see Kruyt, "Colloids", p. 83). Assuming

TABLE VII

INFLUENCE OF THE pH VALUE ON CREAMING OF ORDINARY PLANTATION LATEX, NOT AMMONIATED

Amount of NH_4OH milliequiv. per 100 cc.		pH	DRC	
			Cream	Serum
18		9.17	No creaming, but after 3 days coagulation	
30		9.61	47.8	0.54
42		9.78	49.0	0.75
60		10.14	49.0	0.75
Amount NaOH	Amount NH_3			
2	6	9.35	Creaming, but after 3 days coagulation	
4	6	9.92	50.2	0.55
6	6	10.83	51.3	0.63
8	6	11.6	No creaming	

for the present that the charge is actually the principal factor we find another remarkable resemblance.

When quartz particles are suspended in water and the suspension is allowed to stand, the quartz particles settle to the bottom and occupy a certain volume, the socalled sedimentation volume. Now if an electrolyte is added which decreases the charge on the quartz, the sedimentation volume should increase. If

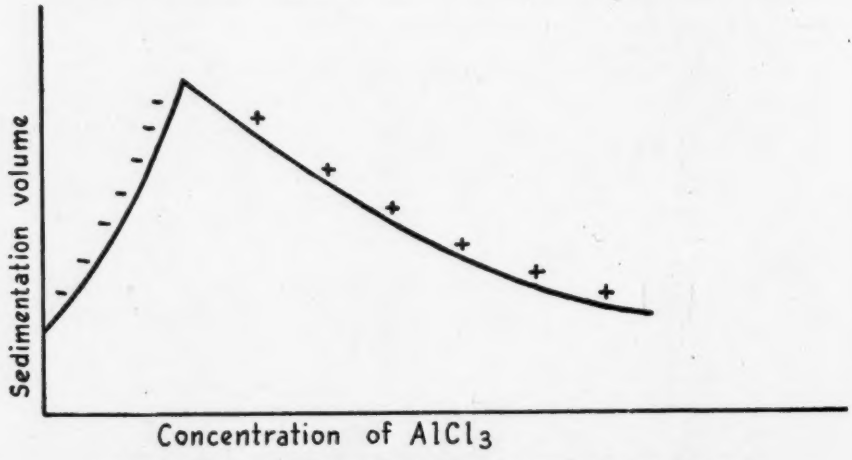

FIG. 10.—Influence of $AlCl_3$ on the sedimentation volume of quartz particles.

an electrolyte such as aluminum chloride is added, which is capable of reversing the charge on the quartz particles, we have the following curve (see von Buzagh, "Kolloidik", p. 172).

Aside from a number of other factors, such as particle size and shape sedimentation, the volume thus depends on the charge carried by the particles. An explanation of this phenomenon[13] must be sought in the assumption that as the charge decreases the ease with which the particles slip past each other also decreases (the cohesive power increases).

In this connection we call attention to the following facts:

1. It has been pointed out by van Dalfsen[14] that the average creaming capacity of latex, regardless of pretreatment, is greater, the lower the viscosity.
2. Substances such as soap and the like, which lower latex viscosity, lead to increased creaming[14].
3. A few preliminary tests show with certainty that the addition of electrolytes increases the viscosity of latex.

That the charge on latex particles has its influence here also is evident from the fact that the viscosity of latex is lower at a higher pH value (ammonia added) than at a lower pH value.

Summarizing, we arrive at these conclusions:

1. An increased charge gives low viscosity and good creaming.
2. A decrease in the charge gives high viscosity and poor creaming.

To explain these phenomena, we have adopted the following hypothesis:

In latex, and most probably also in a majority of emulsions, the particles do not move independently of each other, but exert certain mutual influences. The particles apparently have an inherent tendency to form agglomerates (preagglomeration). This tendency is in fact so strong in the paraffin emulsion which was prepared in the present work that visible agglomerates were formed (see Section V). This preagglomeration increases the resistance to deforming forces (high viscosity). At higher rubber concentrations, *i.e.*, when the particles are situated closer together they impede each other more because of increased viscosity. Finally, when the particles are so close together that they occupy nearly all the space, this hindrance becomes very great, with the result that the viscosity increases rapidly.

Mutual hindrance is diminished by an increase in the charge on the particles and, conversely, it is increased by a decrease in the charge.

In conformity with Twiss and Carpenter, it may be assumed that the addition of a creaming agent results in a linking of the latex particles to the creaming agent molecules, without depriving them entirely of kinetic mobility. Thus it is still possible for them to slip past each other and seek the lowest energy positions (see Section III, C). The smaller the mutual hindrance, the more easily and completely this should be accomplished.

It is self-evident that latex viscosity has some influence on the rate of creaming (cf. van Dalfsen, *loc. cit.*).

The hypothesis now presented, however, explains why the viscosity also influences the creaming equilibrium ultimately attainable.

It is also clear that rapid creaming is connected with the attainment of a high cream concentration.

It may be noted that the viscosity of the latex itself is not so important as the viscosity of the cream layer. This, however, is not strictly true, since the DRC content when between 50 and 60 per cent, has a very strong influence on the viscosity, so that a better criterion of the creaming capacity is available than by viscometry in the less concentrated initial latex, since the DRC content has little influence on the viscosity in that range. Thus viscometric data for cream give more information concerning the internal state of latex.

It is not impossible, however, that the ultimate attainable concentration of cream is subject to a limit imposed by viscosity, *i.e.*, that a certain maximum viscosity cannot be exceeded.

Experimental investigation of this point is one of the objects of our next experimental tests.

IX. FORCES OF REPULSION AND ATTRACTION ON LATEX PARTICLES

In the preceding section we discussed the mutual hindrance of latex particles within certain distances from each other, but without going into detail concerning the nature of this hindrance.

We shall discuss here in a very sketchy way how this hindrance can originate. However, to avoid offering explanations which do not really explain, we must also keep in mind all other phenomena of latex behavior.

It has already been explained that the electric charge carried by a latex particle is governed by the protein molecules adsorbed on the surface, and that this charge is distributed at various points over the surface. Thus the particle is surrounded by an electric field of force, the intensity of which is greatest close to the surface of the particle, and decreases as the distance from the particle increases. The actual course of this intensity as a function of distance may be

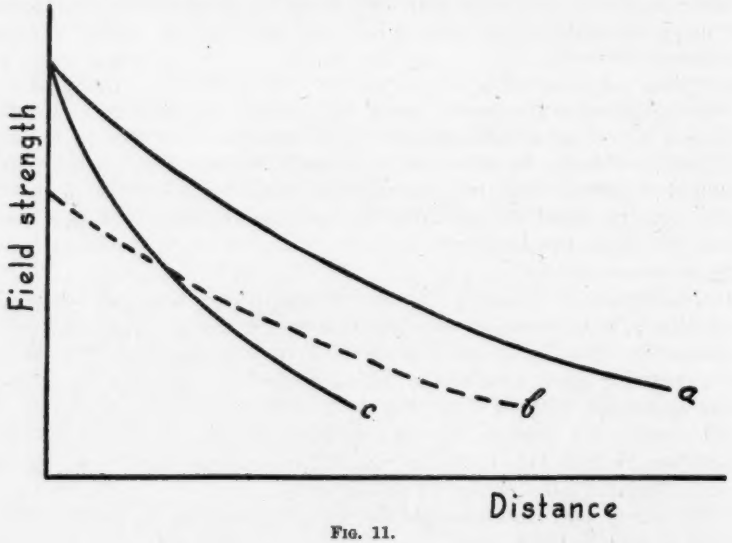

FIG. 11.

disregarded, but it may be supposed that it can be represented by curve *A* in Figure 11.

When the pH value of the medium is decreased, the degree of dissociation of the COOH groups in protein molecules decreases, and consequently the number of negatively charged points also decreases. In that case the course of intensity can be represented, for example, by curve *B* in Figure 11.

When the concentration of electrolyte in the medium is increased at a constant pH value, the distribution of ions around the charged particle (socalled "counterions") changes, with the result that the change in the field intensity is no longer represented by curve *A* but by curve *C* in Figure 11.

In this case the charge at the surface remains the same, but its range of effectiveness is diminished. Now colloid chemical behavior as well as stability and speed of electrophoresis is governed by electrical state, not so much at the immediate surface of the particle as at some distance therefrom. Therefore it is clear that the rate of electrophoresis will be lowered by lowering pH (curve *B*) as well as by adding electrolyte (curve *C*). It is quite common to speak of a

decreased charge for the sake of brevity when what is actually meant is addition of electrolyte. This term, however, is not strictly correct.

Attraction forces, present at the particle surface and inherent in the substance itself, have already been mentioned in discussing cream syneresis. Investigators who have formulated these forces mathematically refer to London and van der Waals forces. These forces also are quite large at the surface of the particle, and become smaller as distance from the particle increases.

Clearly the behavior of colloidal particles is governed by the sum of the forces of repulsion and attraction. It should be noted in such considerations that it is better to use the term "energies" or "potential". It should also be clear that potentials are obtained by integrating field intensity curves.

In lyophilic colloids, we are concerned not only with electrical repulsion but also with repulsion resulting from hydration. In the following discussion we shall refer simply to repulsion energy without any more exact definition.

Figure 12 illustrates the result of combining a repulsion curve with an attraction curve[15]. In this figure the repulsion curve is represented by R and the attraction curve by A. Energies corresponding to A are negative, but curve A is drawn above the abscissas.

Curve T is obtained by combining curves R and A. The significance of curve T is this. When two particles approach each other within a distance which brings them each within the other's sphere of action, their total energy increases. Accordingly they repel each other.

Now suppose that two particles meet with such an impact that their kinetic energy suffices to surmount the energy peak represented by curve T. They will then pass the top of curve T, but quickly thereafter they drop to energy level M. In other words the particles now occupy fixed positions with respect to each other and are pressed together by a large force. This phenomenon is known as irreversible flocculation. Thus it is clear that irreversible flocculation can be effected in various ways; namely:

1. By heating the solution. This imparts such high kinetic energy to particles that, in favorable cases, impact can lead to irreversible flocculation (heat coagulation of latex).

2. By intensive stirring of the solution. This also drives the particles forcibly into contact with each other.

3. By lowering the repulsion curve T to coincide with curves B and C in Figure 11. The normal kinetic energy is then sufficient to carry the particle over the peak. This can be accomplished by lowering the pH value or by adding a salt (latex coagulation by acids and salts). For the sake of completeness it may be added that curve R can also be lowered by decreasing the energy of hydration (latex coagulation by alcohol).

As already stated, the electric charge is distributed in points over the particles. In coagulation the particles must seek those points at which the energy peak is most easily surmounted. This explains why coagulation usually takes some time.

Referring once more to the phenomena of creaming and viscosity, it is evident that the presentation given in Figure 12 is incomplete. Indeed the phenomena which have been discussed give a strong impression that there must be an energy minimum at a substantial distance from the particle, the depth of which is dependent of the electric charge carried by the particles, but which is always flat enough so that the particles are quickly released again.

The concept illustrated by repulsion and attraction curves shows that such a minimum is quite possible.

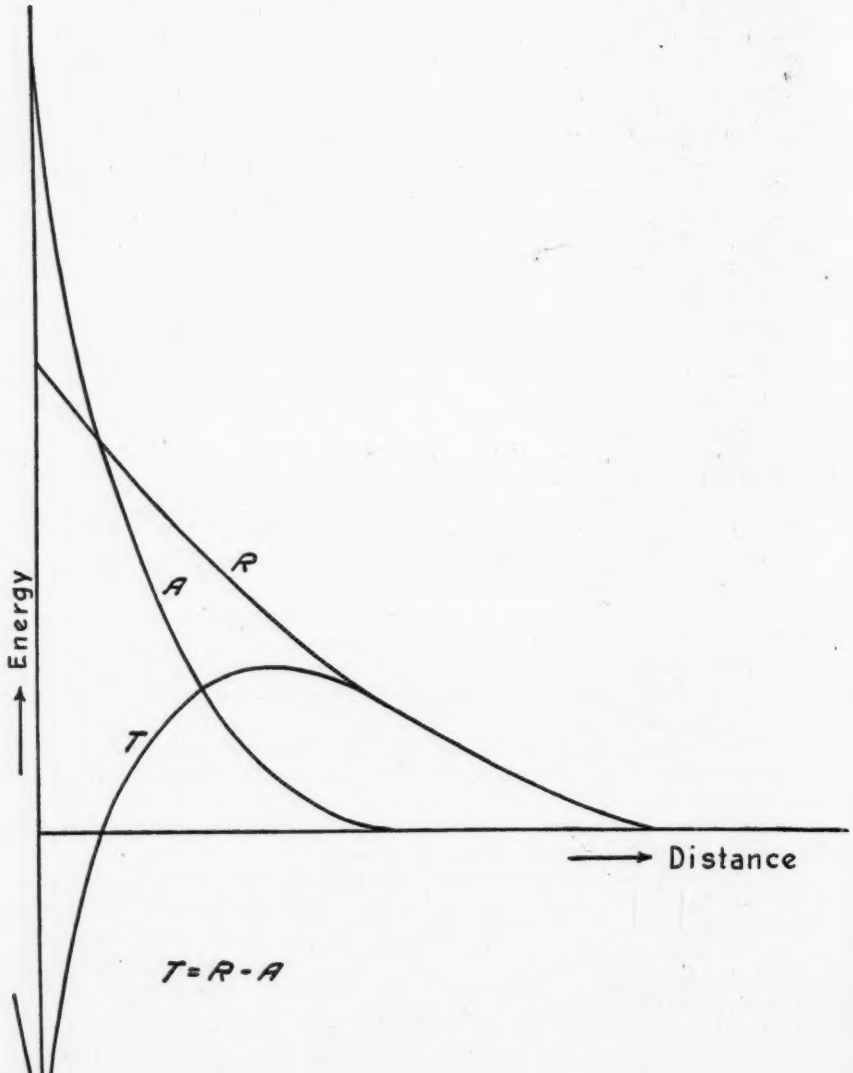

FIG. 12.

The lower the secondary minimum the more difficult is it for particles to escape from each other, that is, the greater is their resistance to repellent forces. In other words, the greater the viscosity the more difficult it is for particles in the cream to slip past each other. Moreover this minimum offers a logical explanation of thixotropy in latex[16].

The low energy level M_2 is responsible for irreversible coagulation phenomena, as indicated in the curves shown in Figure 12.

The problem now is whether reversible cohesion of creaming agent molecules to latex particles must also be attributed to the occurrence of energy minima at a large distance from the particle.

That this cohesion also depends on the charge carried by the particles is evident from the fact that the optimum K flour concentration depends on the concentration of electrolyte (see Section IV, c).

In our opinion it is quite possible that secondary minima are responsible for cohesion between latex particles and the molecules of creaming agent. It should be kept in mind, however, that as for the creaming agent molecules it is only known with certainty that they are negatively charged. For the present it is impossible to discuss the forces of attraction and repulsion on these elongated molecules. Allowance must be made also for the possibility that positive charges must also be formed through the presence of induced or permanent dipoles (this possibility was called to our attention by R. Houwink). As a matter of fact such positive charges could also effect the cohesion of creaming agent molecules to latex.

X. SUMMARY

Section II. The Formation of Agglomerates

Several investigators have already observed the formation of clusters on the addition of a creaming agent to latex (Figures 1 and 2). In strongly diluted latex these clusters migrate individually to the surface of the liquid, thus forming a growing cream layer. Meantime the serum becomes brighter (Figure 3).

In latex of normal concentration the phenomenon is apparently quite different. Here the clusters adhere to each other, forming a network which moves as a whole to the surface of the liquid. So the cream-serum boundary moves upward (Figure 4).

Section III. The Mechanism of Cluster Formation

A. The clusters formed on addition of a creaming agent redisintegrate on dilution with water. Microscopic investigation shows that this redisintegration or redispersion occurs very readily when the cream is "young", but takes a certain, however short time, when the cream is "old" (see Figures 5A and B),

B. When on addition of creaming agent to latex a centrifugal force is applied, the cream layer is formed at once. The density of the cream formed is not so much a function of the magnitude of the centrifugal force applied, as it is of the time elapsing after the addition of creaming agent and centrifuging.

C. The observations under A and B lead to the conclusion that agglomeration or clustering is very loose in the beginning, but with time becomes more compact. A denser cream is formed and serum is expelled.

Independent of Twiss and Carpenter we too come to the conclusion that two phases must be distinguished in the creaming process: a cluster migration and a network shrinkage.

The network shrinkage is called by us cream-syneresis in analogy to other phenomena of that kind and a colloidal explanation is given *mutatis mutandis*.

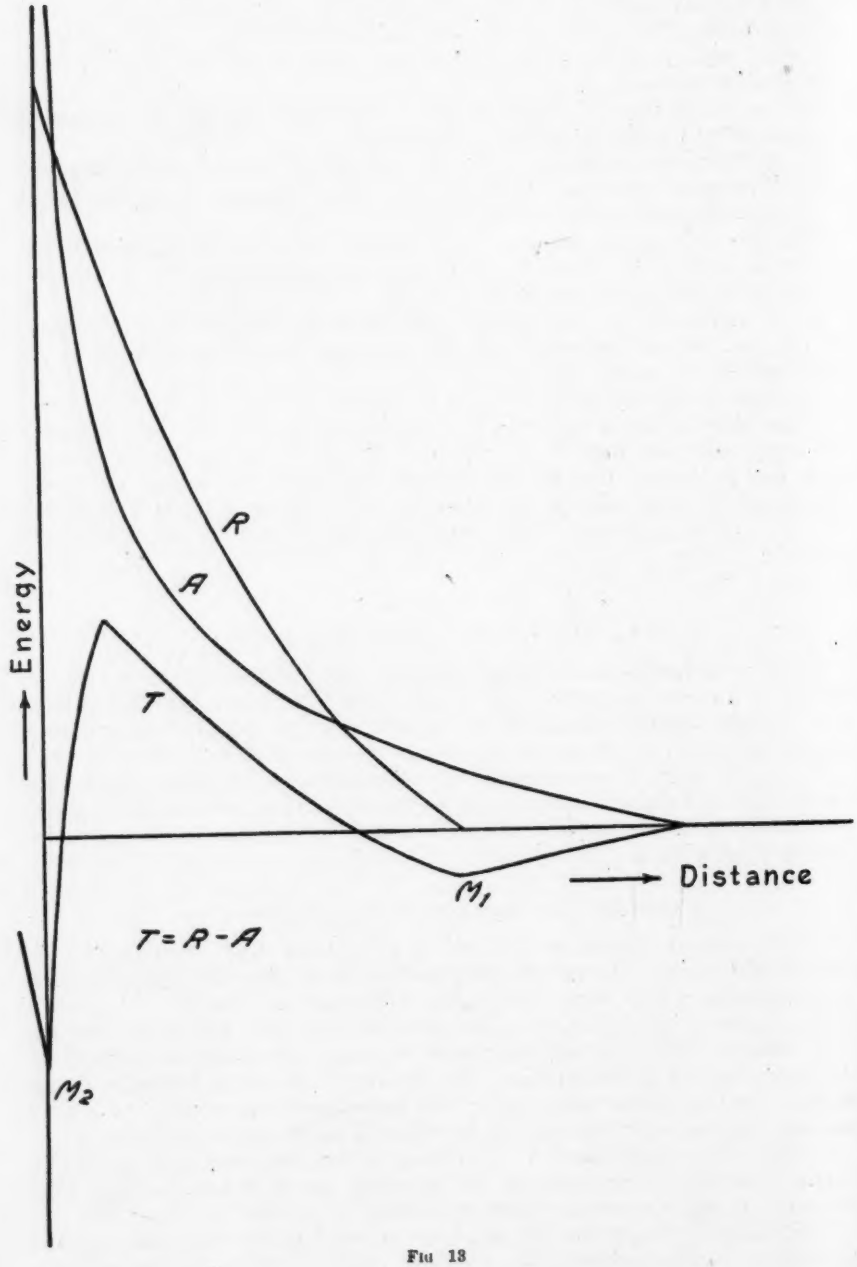

FIG 13

Section IV. Explanation of Cluster Formation

A. The explanation given by Vester is discussed. The formation of a coacervate and the rôle played by the proteins in this process are not in accordance with the facts.

B. The explanation given by Twiss and Carpenter is discussed. The agreement with the facts is fairly good, but the true cause of the anchoring effect needs a closer investigation.

C. Attention is drawn to the mirror process of creaming, the sedimentation of coalwashery effluent. The mechanism of this process may be similar to the mechanism of the creaming process.

Section V. Influence of the Concentration of the Creaming Agent on the DRC Content of Cream and Serum

On increasing the amount of creaming agent, the serum becomes brighter, but the DRC content of the cream decreases. This is not restricted to latex, because on creaming a paraffin emulsion similar phenomena are experienced (Figure 6).

The amount of konnyaku flour which gives the best creaming depends on the concentration of the latex (Figure 7).

Section VI. The Influence of Electrolytes on the DRC Content of Cream and Serum

A. Experiments with dialyzed latex of low protein content show that, on increasing the concentration of electrolytes, the DRC content of the cream generally drops. At the same time the DRC content of the serum drops too (Figure 8).

B. Dialyzed latex of normal protein content behaves in a similar way, but the influence of electrolytes is less pronounced (Table III).

C. A paraffin emulsion shows similar phenomena.

Section VII. The Influence of the pH Value on the DRC Content of Cream and Serum

Creaming is only possible between certain intervals of the pH value. At lower and at higher hydrogen ion concentrations, the DRC content of the cream rapidly decreases.

Section VIII. Discussion of the Results

The phenomena described in Sections VI and VII show that the electric charge of the latex particles has a large influence on the creaming capacity. Factors affecting this charge (electrolytes and pH value) affect also the creaming capacity of the latex.

Attention is drawn to the analogous behavior of quartz particles when settling in water containing different amounts of aluminum chloride (Figure 10).

The sedimentation volume is small when the electric charge of the particles is high. An explanation given is that, when the electric charge decreases, the tendency of the particles to adhere increases (Von Buzagh: "Haftfähigkeit").

Attention is drawn to the following facts:

1. Van Dalfsen has shown, that the mean creaming capacity of latex is higher when the viscosity is lower.
2. Chemicals lowering the viscosity of latex, *e.g.*, soap, increase the creaming capacity.
3. We have found that the addition of electrolytes (lowering the charge of the particles) increases the viscosity of latex.

When the charge is increased by addition of ammonia, the viscosity is lowered.

Summarizing, we come to the following conclusions:

1. Increased electric charge gives low viscosity and good creaming.
2. Decreased electric charge gives high viscosity and poor creaming.

To explain all these phenomena, we assume that in latex, and probably in most concentrated emulsions, the particles do not move independently, but exert a certain influence on each other (hindering effect or tendency to agglomeration). The higher the concentration of the latex, the greater the hindering forces, and the greater the viscosity. The higher the charge of the particles, the higher the repulsive forces, the lower the hindering forces, and the lower the viscosity.

In accordance with Twiss and Carpenter, we assume that on addition of creaming agent the latex particles are chained together by the molecules of the creaming agent without losing all their kinetic mobility. So they are able to slide along each other and to occupy positions with the lowest energy; these can be reached better and easier when hindering forces are smaller.

It is now clear why viscosity not only influences the velocity of creaming, but also the DRC content of the cream obtained.

Section IX. Repulsive and Attractive Forces at the Surface of a Latex Particle

To explain the hindering forces of the particles, mentioned in the preceding chapter, a general theory is developed based on the views of Hamaker, regarding attractive and repulsive forces at the surface of a colloidal particle.

The theory can explain the irreversible phenomena as coagulation by acids, electrolytes, alcohol, heat and mechanical forces as well as the reversible phenomena, *i.e.*, the mutual hindering of the particles at fairly large distances from each other and the formation of clusters on addition of a creaming agent.

REFERENCES

[1] Kraay, Concentrating latex by creaming, *Bergcultures*, **7**, 1123 (1933).
[2] Kraay, *Bergcultures* **13**, 1044 (1939).
[3] Baker, Trans. *Inst. Rubber Ind.* **13**, 70 (1937).
[4] Twiss and Carpenter, *Proc. Rubber Tech. Conf. London*, **1938**, 81.
[5] Vester, *Arch. Rubbercultuur* **22**, 145 (1938).
[6] Twiss and Carpenter, see note 4.
[7] McBain, *J. Phys. Chem.* **30**, 239, 313 (1926).
[8] van Iterson, *Proc. Royal Soc. Amsterdam*, **41**, 81 (1938).
[9] Overbeek, "Symposium on Hydrophobic Colloids", **1937**, 130 de Boer, *Chem. Weekblad* **35**, 122 (1938).
[10] van Gils, *Arch. Rubbercultuur* **23**, 29 (1939).
[11] Hauser and Bender, *Proc. Rubber Tech. Conf. London*, **1938**, 7.
[12] Kemp and Twiss, *Trans. Faraday Soc.* **23**, 89 (1936), *India-Rubber J.* **93**, 10 (1937).
[13] Ehrenberg, "Bodenkolloide", Dresden **1922**, 83.
[14] van Dalfsen, *Arch. Rubbercultuur* **23**, 1 (1939).
[15] Hamaker, "Potential curves as a basis for the discussion of colloid phenomena", Symposium on Hydrophobic Colloids, Utrecht **1937**, 16.
[16] Freundlich, "Thixotropie", Paris, **1935**, 19.

THE PRESERVATION OF LATEX BY STERILIZATION IN THE PRESENCE OF A BUFFER SOLUTION *

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It is well known that commercial latex is preserved with either a fixed alkali such as caustic potash or a volatile alkali such as ammonia, although various objections may be cited against each of these types of material. The fixed alkali remains in the rubber if the latex is dried by evaporation and may affect materials with which it comes into contact, or it may introduce other features, such as an increase in the water-absorption capacity of the rubber. On the other hand the volatility of ammonia is objectionable to operatives on account of its odor; it has to be removed by air-blowing before the latex can be utilized in certani processes, otherwise inferior products are obtained; it is also relatively expensive to the producer.

For these reasons the problem of finding alternative materials as preservatives of latex has occupied the attention of the producers' research organizations for a considerable time, and the properties of a number of bactericides have been investigated in the laboratories of the Rubber Research Institute of Malaya. The results of these investigations have been published periodically in *The Journal of the Rubber Research Institute of Malaya.*

It was found by Rhodes[1] that materials such as the alkyl salts of mercury, compounds of arsenious oxide and the sodium salts of chlorinated phenols are efficient preservatives of *Hevea* latex, but in all cases only if a small amount of ammonia is present to raise the pH of the latex to the neighborhood of 8.0, or alternatively if a sufficient quantity of the preservative is used, as in the case of sodium pentachlorophenate, to attain approximately the same pH value. Owing to their poisonous nature the use of some of the materials mentioned above is impracticable, but sodium pentachlorophenate is known to have commercial possibilities.

Spence[2] has criticized the use of alkalies, such as ammonia, on the grounds that "they merely delayed or lessened the natural tendency of fresh latex to decompose and coagulate without eliminating the cause for those chemical and physical changes which find their expression in the constantly changing properties of the final coagulum". He added that "latex is still far from being a stable article of commerce and there are many practical difficulties in connection with its use". Presumably in support of the above, Spence used the following extract from an address by Rhodes[3] before the Rubber Section of the American Chemical Society: "When latex is won from a tree under practical conditions, it is contaminated by bacteria. This contamination cannot be prevented in practice. . . . . The acidity which the bacteria produce causes premature coagulation in the field, which can be prevented by the addition of small quantities of either sodium sulfite or ammonia. But the amounts in which they are used are not

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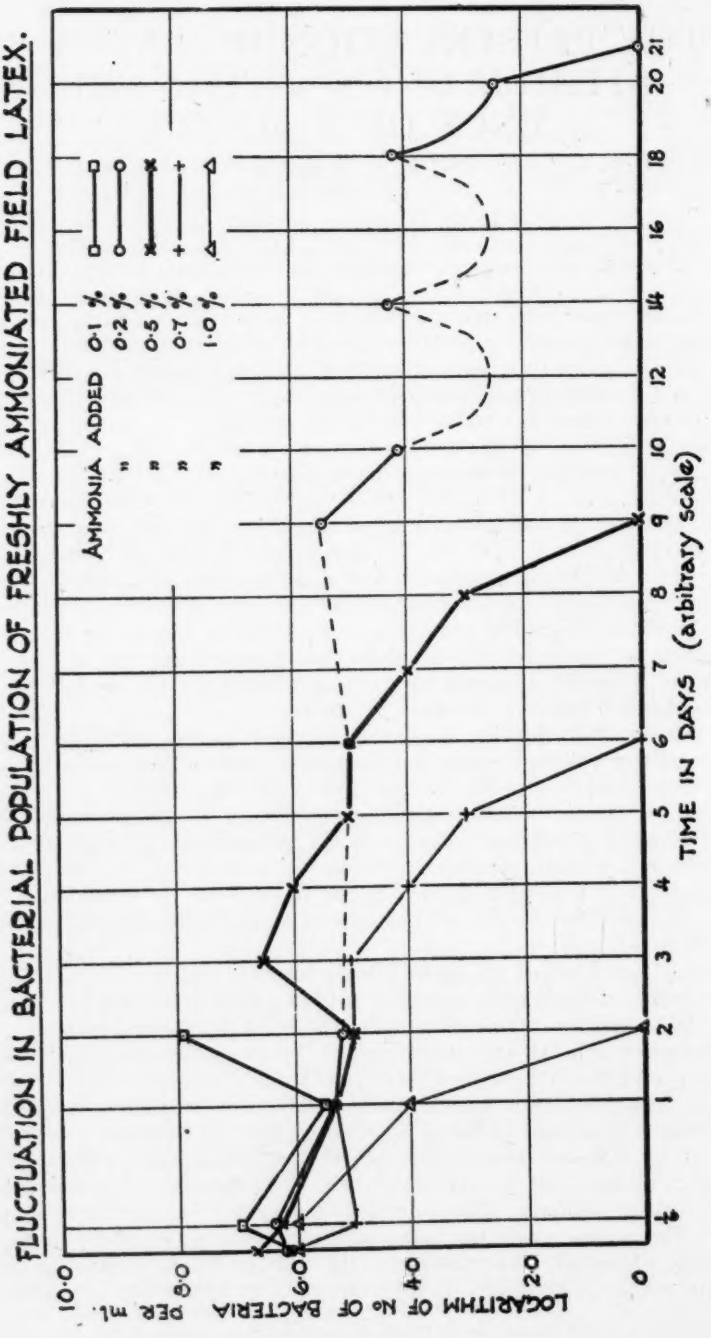
FLUCTUATION IN BACTERIAL POPULATION OF FRESHLY AMMONIATED FIELD LATEX.
AMMONIA ADDED 0·1 %
" 0·2 %
" 0·5 %
" 0·7 %
" 1·0 %
LOGARITHM OF No OF BACTERIA PER ml.
10·0
8·0
6·0
4·0
2·0
0
½ 1 2 3 4 5 6 7 8 9 10 12 14 16 18 20 21
TIME IN DAYS (arbitrary scale)

FIG. 1.

sufficient to kill the bacteria. *They do not sterilize the latex, and although the latex may appear to be satisfactory, the bacteria are still at work, producing decomposition in the latex components.* Varying degrees of bacterial contamination and activity from day to day can, therefore, make only for a further adventitious variability in latex composition".

The italics in the above quotation are Spence's, and the inference which one might draw is that active bacteria are present in all ammonia-preserved latex, whereas the above extract refers to latex treated in the field with small quantities of ammonia insufficient to sterilize the latex. The existence of bacteria in latex depends on the extent of ammoniation, and although periodical infection may occur through contact with the atmosphere, if it is adequately preserved, bacteria cannot survive and for practical purposes sterility is maintained.

TABLE I

BACTERIAL POPULATION (IN THOUSANDS) PER CC. OF LATEX PRESERVED WITH VARIOUS QUANTITIES OF AMMONIA

Days after preservation		Latex A		Latex B		Latex A
		Ammonia (per cent)				
		0.1	0.2	0.5	0.7	1.0
0	11 a. m.	1,300	1,500	5,000	1,300	1,000
	3 p. m.	9,000	2,500	2,000	100	1,000
1		300	200	200	200	<10
2		83,600	150	100	100	0
3		Coagulated	<100	3,300	100	Sterile
4			<100	1,000	10	
5			<100	100	1	
6			<100	100	0	
7			<100	10	Sterile	
8			30	1		
9			13	0		
10			<1	Sterile		
11			<1			
12			<1			
13			20			
14			<1			
15			<1			
16			<1			
17			16			
18			<1			
19			0.3			
20			0			
21			Sterile			

Data taken from our records showing the fluctuations in the bacterial populations of 1 cc. of latex in the period after collection and preservation with different amounts of ammonia are shown in Table I and also in Figure 1, in which the logarithms of the bacterial populations are plotted. The figures in the columns of Table I under 0.1, 0.2 and 1.0 per cent ammonia were derived from identical latex (A) taken from the same task at the same time. This was a latex having a low initial bacterial population. On the other hand, the figures in the columns under the headings 0.5 and 0.7 per cent have been obtained from an average type of field latex (B), with an infection higher than A at the time of ammoniation.

In the case of latex A, 0.1 per cent ammonia was insufficient to prevent a large outburst of bacterial activity on the third day, resulting in coagulation. With 0.2 per cent ammonia, a small increase in bacterial content occurred on the afternoon of the day of collection, and it will be observed that renewed activity oc-

curred on the fourteenth and eighteenth days before sterility was attained after 21 days. If this latex had had a higher initial infection, produced, for example, by delaying ammoniation, the initial outburst would have been greater and probably would have resulted in early coagulation. This is illustrated in the case of latex B, preserved with 0.5 per cent ammonia. Here the initial infection was higher, and there was a relatively larger outburst of activity on the fourth day before sterility was attained on the tenth day. Larger amounts of ammonia prevent this activity, as shown in the examples of the latex preserved with 0.7 and 1.0 per cent, where, apart from a relatively small increase in the case of the former on the second day, a gradual decrease in bacterial numbers occurred, and sterility was attained on the seventh and third days, respectively. Changes were observed by Beeley[4] in the bacterial population of a bulked estate latex which was not very clean and in which further contamination, possibly from the collecting buckets and other utensils, caused an even greater increase in bacteria numbers, attended by a greater accentuation of the bursts in bacteria development. In such cases the risk of coagulation after ammoniation is correspondingly greater, particularly if only a small amount of ammonia is added. Hence the recommendations to producers to use not less than 0.70 per cent ammonia for the preservation of estate latex.

The sterility of efficiently preserved latex is confirmed also by the small quantitative changes which take place in its components over a period of storage. It has been ascertained that the changes in rubber and ammonia contents over a period of storage are very small (unpublished London Advisory Committee Report) Davey and Coker[5] have shown that a latex having an original ammonia content of 0.77 per cent and a dry-rubber content of 36.2 per cent had, after keeping for one year, an ammonia content of 0.79 per cent and a dry-rubber content of 35.8 per cent. The change in the dry-rubber content is negligible compared with that which takes place when rubber is broken down into "water-soluble products" by mould. Bishop and Fullerton[6], however, observed an appreciable change in ammonia content during a similar period when the latex was not sterile.

It is realized that considerable changes in the stability of latex take place during storage, justifying to some extent the description that it is not a "stable article of commerce". The stability of latex increases during a period of several months after preparation, and then gradually decreases. These changes are not a result of the presence of active bacteria, but are caused by the presence of ammonia, of naturally occurring enzymes, or of enzymes formed *in situ* from bacteria before the latter are destroyed, each of which may react with the non-rubber substances, gradually altering the nature of the protective coating on the rubber particles. Moreover evidence has been accumulated by Roberts[7] to show that the changes which occur in latex are very marked in the period subsequent to ammoniation and, further, that it is the natural variation inherent in a plant product such as latex which causes the chief difficulties to the manufacturer during processing.

Spence sought to eliminate "the objectionable changes known to develop in ammonia-preserved latex and to produce a stable product, free from the practical difficulties resulting from the presence of alkali in latex" by investigating the factors which affect the stability of *Hevea* latex deammoniated by dialysis, and by making studies with latex from the *Guayule* plant. The method adopted was to buffer the latex with a solution of M/20 sodium dihydrogen phosphate containing the requisite amount of M/20 caustic soda to produce a mixture having a pH of approximately 7.0. It was shown that "the stability of the latex was largely dependent on its reserve buffer strength, and that by increasing this

strength by the use of an artificial reserve of buffer solution having the same pH as that of the latex itself, the stability of the latex could be maintained over a prolonged period of time without coagulation taking place; that fresh latex adequately buffered in this way could be heated to temperatures well above those employed in modern bacteriological practice without coagulation ensuing. These observations paved the way for a permanently stable and neutral sterile latex".

A method claiming such results must command the attention of those interested in the preservation of latex. The method claims to eliminate the use of alkalies and bactericides, either or both of which have hitherto been and, in view of the experiments described below, still are considered indispensable for the satisfactory preservation of latex. It is uncertain as to how far experiments were made with fresh latex, but in view of the statements that "sterile latex prepared in the East remained uncoagulated as far as it is possible to determine" and later that "at long last fresh *Hevea* latex can be shipped to any part of the world", the authors felt justified in assuming that the method was suitable for the preservation of fresh latex, and have endeavoured to ascertain if this process has any commercial possibilities.

EXPERIMENTAL

The buffer solution was prepared by adjusting the proportions of M/20 solutions of caustic soda and sodium dihydrogen phosphate to obtain a solution of pH 7.0. The proportions required were found to be 500 cc. of M/20 NaH_2PO_4,H_2O and 230 cc. of M/20 NaOH, and therefore 1 cc. of buffer solution contained 0.00473 gram of NaH_2PO_4,H_2O and 0.00630 gram of NaOH.

Various proportions of the buffer solution were added to 100-cc. units of fresh latex (d.r.c. 38 per cent) from the Rubber Research Institute Experiment Station, and the mixtures (1) were allowed to stand without having been heated, and (2) were heated in an air oven for 2 hours at 100° C. In every case after standing for a period of 24 hours the mixtures showed a tendency to coagulate or curdle and were very unstable.

The particulars of the mixtures used are shown in Table II.

TABLE II

Date	Sample No.	Volume latex (cc.)	Volume buffer (cc.)	NaH_2PO_4, H_2O in mix (Per cent)	NaOH in mix (Per cent)
2.3.39	1	100	10	0.0430	0.0057
"	2	100	20	0.0788	0.0105
"	3	100	30	0.1014	0.0145
"	4	100	40	0.1351	0.0180
"	5	100	50	0.1576	0.0210
"	6	100	60	0.1773	0.0236
"	7	100	70	0.1948	0.0260
"	8	100	80	0.2102	0.0280
"	9	100	90	0.2240	0.0298
"	10	100	100	0.2365	0.0315

A second series of samples were prepared, one-half of which was stored at room temperatures and the other half heated in an autoclave at 15 lbs. pressure for 20 minutes. Again the resultant mixtures were unstable, and either clotted or coagulated within a short time. It appears that the method is unsatisfactory for the preservation of fresh latex with the quantities of buffer solution used. With the larger amounts of buffer solution it was observed that coagulation was not so

marked, probably due to the dilution effect. The addition of still larger amounts would necessitate further dilution, and would therefore be outside the bounds of practical considerations.

The data relating to the second series of experiments are shown in Table III.

TABLE III

Sample No.	Volume latex (cc.)	Volume buffer (cc.)	NaH_2PO_4, H_2O in mix (Per cent)	NaOH in mix (Per cent)	pH mix	Condition on storage	
						Not sterilized	Sterilized
1	100	25	0.0946	0.0126	6.5	Coagulated next day	Clotted on autoclaving
2	100	50	0.1576	0.0210	6.6	do.	do.
3	100	75	0.2028	0.0270	6.6	do.	do.
4	100	100	0.2365	0.0315	6.6	do.	do.

Spence has stated that the variation which occurs in the pH of latex of the same species is slight and, in the case of *Hevea* latex, does not extend beyond the range of substantial neutrality. There is by no means unanimity as to the actual pH of fresh latex, values ranging from 5.8 to 7.2 having been indicated by different workers, *e. g.*, Belgrave[8], Bobilioff[9], Hauser and Scholz[10], and van Harpen[11]. This variation is due probably to the use of different methods of determination rather than to inherent differences in *Hevea* latex from different sources. The pH of the latex used in the experiments above (Table III) was 6.5 (determined by the glass electrode), and to simulate Spence's conditions it was brought nearer to neutrality by the addition of a small amount of ammonia.

Three samples of latex thus treated were buffered and sterilized in a manner similar to that of the previous series. The results are shown in Table IV.

TABLE IV

Sample No.	Volume latex (cc.)	Volume buffer (cc.)	NaH_2PO_4, H_2O in mix (Per cent)	NaOH in mix (Per cent)	pH mix	Condition on storage	
						Not sterilized	sterilized
1	100	25	0.0946	0.0126	6.9	Coagulated in 1 day	Coagulated on autoclaving
2	100	50	0.1573	0.0210	6.9	Coagulated in 1 day	Coagulated on autoclaving
3	100	100	0.2365	0.0315	6.9	Coagulated in 1 day	Curdy after 12 days

Sample No. 3, autoclaved, was still fluid after seven days, and on opening the container, it was observed that the latex was also sweet. After a further five days, however, the latex clotted, probably owing to its being nonresistant to bacteria which were admitted when the container was opened. The results of this series were therefore slightly less unsatisfactory than those of the unammoniated samples, but could not be considered of practical value.

It is known that ammoniated latex, even after deammoniation, behaves in many ways differently from fresh latex. Complete deammoniation of latex is difficult, but it was considered advisable to ascertain the effect of the sterilization-buffer process on this type of latex, as used by Spence. Latex which had been stored for two months was deammoniated to a methyl red titer of 0.03 per cent, and subsequently sterilized (autoclaved) after buffering with various amounts of buffer solution. The results are shown in Table V.

The results shown in this series are not so unsatisfactory as those of the previous series. All the latices were in a fairly good condition after storage for periods up to 3 weeks, but after this they showed signs of deterioration, and after 4 weeks all the samples had coagulated. It was observed also that the buffered deammoniated latices were not superior to the unbuffered deammoniated latices, indicating that buffering was not of material value.

As a result of these experiments the following general conclusions are drawn.

(1) That diluted fresh latex, buffered or unbuffered, is more resistant than concentrated latex to clotting and coagulation on sterilization by autoclaving.

(2) That deammoniated latex is more resistant than fresh latex to clotting or coagulation on sterilization by autoclaving.

(3) That buffered latex sterilized by autoclaving is not resistant to bacteria, and is therefore unstable and coagulates when exposed to infection. All the samples described above would be contaminated when the containers were opened and the contents examined periodically.

TABLE V

Sample No.	Volume latex (cc.)	Volume buffer (cc.)	NaH_2PO_4, H_2O in mix (Per cent)	NaOH in mix (Per cent)	pH mix	Condition on storage	
						Not Sterilized	Sterilized
Control							
1	100	0	0	0	7.3	Coagulated in 2 days	Coagulated in 4 weeks
2	100	25	0.0946	0.0126	7.8	Coagulated in 2 days	Clot present in 4 weeks
3	100	50	0.1576	0.0210	8.0	Coagulated in 2 days	Big clot in 4 weeks
4	100	75	0.2028	0.0270	7.7	Coagulated in 2 days	Very big clot in 4 weeks
5	100	100	0.2365	0.0315	7.5	Coagulated in 2 days	Big clot. Bad smell in 4 weeks

Spence[12], in a notable contribution to the subject of the preparation from plantation rubber of a modified rubber with improved oil-resistant properties, mentions the determination of the amounts of sol and gel fractions of latex buffered and sterilized in sealed containers immediately after collection in the Far East. Some of this latex was stated to be three years old, and it is presumed that it had been kept in the sealed containers during this period to retain its fluidity. Such conditions would be difficult to attain in commercial practice and, in view of the observations recorded above, it is concluded that the method is of academic interest only, and that it would have no value as a practical method for the large-scale preparation and shipment of latex from the producing countries.

The authors acknowledge the assistance given by K. C. Sekar in carrying out some of the practical work described above.

SUMMARY

A method of preserving latex has recently been suggested by Spence which consists of the sterilization of latex by autoclaving in the presence of a buffer reagent. In view of the improved properties claimed for the material, together with the lower cost of production, both of which are of interest to producers of latex, the method has been investigated. It is concluded that the process is not of value as a practical method for the commercial preservation of fresh *Hevea* latex.

REFERENCES

[1] Rhodes, *Annual Report Rubber Research Inst. Malaya* **1935**, 122.
[2] Spence, *Rubber Age* (N. Y.) **44**, 81 (1938).
[3] Rhodes, *Ind. Eng. Chem.* **27**, 1205 (1935).
[4] Beeley, *Annual Report Rubber Research Inst. Malaya* **1934**, 110.
[5] Davey and Coker, *Trans. Inst. Rubber Ind.* **13**, 368 (1938).
[6] Bishop and Fullerton, Rubber Research Inst. Malaya, Planting Manual No. **4**, p. D. 8 (1932).
[7] Roberts, *J. Rubber Research Inst. Malaya* **8**, 192 (1938).
[8] Belgrave, *Malayan Agr. J.* **11**, 362 (1933).
[9] Bobiloff, *Arch. Rubbercultuur* **8**, 609 (1924).
[10] Hauser and Scholz, Kautschuk **3**, 304 (1927).
[11] van Harpen, "The Electrometric Determination of the Hydrogen Ion Concentration in the Latex of Hevea Brasiliensis and its Applicability to Technical Problems," Varekamp & Co., Medan, **1930**, p. 42.
[12] Spence, *J. Soc. Chem. Ind.* **58**, 345 (1939).

ELASTIC RECOVERY AND PLASTIC FLOW IN RAW RUBBER *

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1. PURPOSE OF THE WORK

A satisfactory theory of the structure of raw rubber must be able to account for all the physical phenomena displayed by this material. It is of importance, therefore, that its physical behavior should be carefully studied and described in the most direct and accurate manner possible. Experimental studies of this kind may also be of assistance in suggesting the most hopeful lines of approach to the theoretical study of the problem[1].

The first specific problem which appeared to require examination was that of the separation of the elastic and plastic effects which in general take place simultaneously when raw rubber is subjected to deformation. The existing information on this subject is scanty. True, numerous studies of plasticity have been carried out, but these have been concerned almost entirely with masticated rubber, with which it is not proposed to deal here. Stress-strain curves for raw rubber at different temperatures have been given by Rosbaud and Schmid[2]. In contrast to those for vulcanized rubber, these show a great dependence on the temperature and on the rate of extension, effects which have generally been attributed to the occurrence of plastic flow, although the magnitude of the flow has not been determined. On the other hand, several workers, including in particular Feuchter[3], have drawn attention to the fact that raw rubber, when stretched quickly to about 600% elongation, recovers on warming practically to its original length, *i. e.*, there is no plastic flow in this case. Perhaps the most successful attempt to distinguish the plastic from the elastic deformation was made by Whitby[4], who clearly demonstrated the kind of difficulty encountered in an investigation of this kind. Whitby maintained specimens of raw rubber extended to a constant length for given times at various temperatures. They were then allowed to recover for several days at room temperature, until the length had ceased to change, but on subsequently raising the temperature to 100° C a further contraction was observed. The "set" remaining after this treatment was regarded as a plastic deformation. This view will be shown not to have been entirely justified.

In the present work Whitby's methods have been taken as a starting-point, but greater care has been exercised in securing the complete removal of elastic strain. The data cover the following aspects of the behavior of rubber:

1. The elastic recovery at constant temperature.
2. Further recovery on raising the temperature.
3. The nonrecoverable extension or plastic flow.
4. The decay of tension at constant extension.

Finally an attempt is made to draw certain inferences concerning the structure of raw rubber from the results of these experiments.

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2. EXPERIMENTAL METHODS

The rubber used in these experiments was Malayan crepe. Its average molecular weight (M) was determined from viscosity measurements in dilute benzene solutions. The ratio of specific viscosity (η_{sp}) to concentration (c), expressed in g. per 100 cc. solution, extrapolated to infinite dilution was 7.0. Applying Staudinger's equation:

$$k\,\frac{\eta_{sp}}{c} = M$$

and assuming his value[5] of the constant k for rubber, *i. e.*, 22,000, a figure of 154,000 was obtained for the average molecular weight.

Preparation of Specimens.—One difficulty experienced in working with raw rubber is to obtain the material in a form suitable for carrying out mechanical tests. For this purpose it is important that the rubber should be of uniform texture and thickness. In these respects crepe in its commercial form is unsuitable. To overcome this difficulty, films were prepared by pouring a 4% solution of the rubber in benzene onto a flat surface and drying off the solvent. In the first attempts the solution was poured into a frame standing on a glass

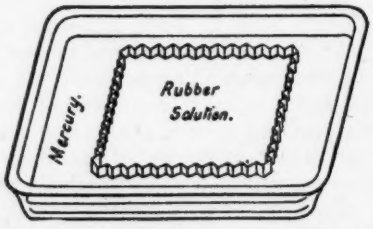

FIG. 1.—Preparation of rubber films from solution.

plate, but films prepared in this way were found to be in a state of internal strain which arose from the inability of the solvent-swollen rubber to contract freely during drying, owing to its adhesion to the glass. This was a serious difficulty, for the strain thus introduced could not easily be removed, and it is clearly of the utmost importance in experiments of the kind contemplated that the material worked on shall be strain-free initially. The difficulty was overcome by pouring the solution onto a mercury surface with a confining boundary consisting of a zig-zag paper strip floating edgewise on the mercury, as depicted in Figure 1. Such a boundary offers no appreciable resistance to uniform contraction of the film during drying, the contraction actually obtained amounting to 35% of the linear dimensions. Films prepared by this process were practically strain-free, judged by the methods to be described later.

From the films thus prepared, whose thickness was in the neighborhood of 0.3 mm., straight test-pieces 40 mm. long and 5 mm. wide were cut. In the experiments a free length of 30 mm. between grips was used, measurements being taken on a marked length of 10 mm. in the middle of the specimen.

The Stretching Machine.—The essential details of the stretching machine employed are shown in Figure 2. The upper grip G_1 was hung by a steel wire from the flat steel spring S, the deflection of which could be read on the scale C. The lower grip G_2 was connected by a cord passing round pulleys P_1, P_2, P_3 to the 1 kg. weight W. The release of this weight by means of the trigger T

caused a rapid extension of the test-piece. The supporting rod R was of glass, a material preferred to metal on account of its lower thermal conductivity. The specimen could be surrounded by a tube A, which was immersed in a constant-temperature bath. In no case was liquid used in direct contact with the rubber.

By this arrangement the tension could be observed while the specimen was stretched approximately to a constant length. There was, of course, a small change of length due to the movement of the spring, but this was not more than 2% of the stretched length of the specimen during any experiment.

In carrying out the experiments the unstretched specimen was inserted in the thermostat and, after a suitable warming-up time, the weight was released. Commencing 5 seconds after releasing the weight, readings of tension were taken at

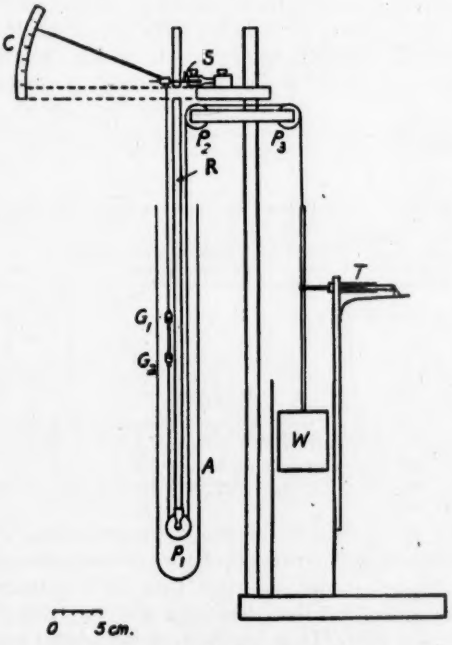

FIG. 2.—The stretching machine.

suitable intervals throughout the period of extension. At the end of this time the stand was lifted so as to remove the specimen, still stretched, from the thermostat, and an interval, generally 5 minutes, was allowed for the rubber to cool down below 25° C. The tension was then released, the lower end of the specimen cut off below the marking to remove unnecessary weight, and the specimen transferred to the 25° C thermostat. Subsequent changes of length were then noted over a 20-hour period.

3. THE REMOVAL OF STRAIN FROM STRETCHED RUBBER

The general nature of the recovery phenomena observed after raw rubber has been stretched is shown in Figure 3, curve (*a*), which depicts the behavior of a specimen of crepe after stretching at 50° C for 1 hour at an elongation of 390%.

At 25° C there was an immediate recovery to 260% elongation on releasing the tension. Thereafter there was a further recovery, rapid at first, then progressively slower, over a period of 20 hours. Increasing the temperature to 50° C caused a sharp increase in the rate of recovery, but with continued heating the rate again slowly diminished. At 100° C the same phenomenon was repeated. Even then the elastic recovery was not complete. For the further removal of strain two methods were tried, both depending on the swelling action of a solvent. In the first method the specimen was hung in a vessel containing some benzene and the vapor allowed to act on the rubber for a certain time, after which it was removed and dried. The permissible swelling was limited by the tendency of the rubber to sag, so that several successive treatments were usually necessary to secure constancy of length. In the second and preferred method the rubber was immersed in a liquid benzene-alcohol mixture, removed after a suitable time, and dried. This method avoids the sagging difficulty and also permits of a control over the amount of swelling by variation of the benzene content of the mixture. The results obtained by the two methods were in close agreement.

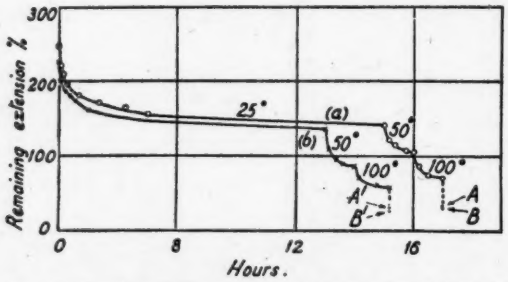

FIG. 3.—Elastic recovery of crepe at temperatures indicated after stretching to 390% extension for 1 hour at 50° C.

(*a*) Normal.
(*b*) Vacuum-treated.

In Figure 3 point A represents the remaining extension after treatment for 16 hours by a mixture containing equal volumes of benzene and alcohol. Point B represents further treatment for the same time by a mixture containing 60% of benzene. It will be noted that these treatments led to a reduction of the residual extension by more than 50%. It is hardly possible to use a mixture containing a higher percentage of benzene, owing to the difficulty of handling such highly swollen rubber. However, since the effect of the 60% mixture was not very much greater than that of the 50% mixture, it may be assumed with some confidence that the final length of the rubber represents, if not a complete removal of elastic strain, at least a close approach to that condition. The remaining extension may therefore be regarded as a genuine plastic flow.

Possible Effects Due to Retained Solvent.—The preparation of specimens from solutions is open to the criticism that there might be a trace of solvent left in the rubber even after several days' drying at room temperature, the presence of which might seriously affect the mechanical properties. To meet this criticism a piece of rubber prepared in the usual way was heated to 50° C for 8 hours in a high vacuum, with liquid air applied to the evacuated tube, a treatment which should have been sufficient to remove any remaining solvent. The rubber was stretched at 50° C by means of a falling weight, and the recovery was observed first at 25° C and then at higher temperatures, both the stretching and

recovery being completed without admitting air to the tube. The rubber was then removed and treated with benzene-alcohol mixture in the usual way. The result of this experiment is shown in Figure 3, curve (*b*), from which it is clear that the precautions taken made no marked difference either to the amount of the elastic recovery at any temperature or to the plastic flow, and it may therefore be concluded that the results reported are not in error on account of absorbed solvent. At the same time this experiment proves that the possible presence in the rubber of water absorbed from the atmosphere was not having an important effect.

4. THE PHENOMENA OF ELASTIC RECOVERY

Recovery at 25° C after Stretching at 25° C.—Figure 4 shows the recovery curves obtained at 25° C for samples stretched for 1 hour at 25° C to various elongations. Noteworthy features of these curves are that for the higher elonga-

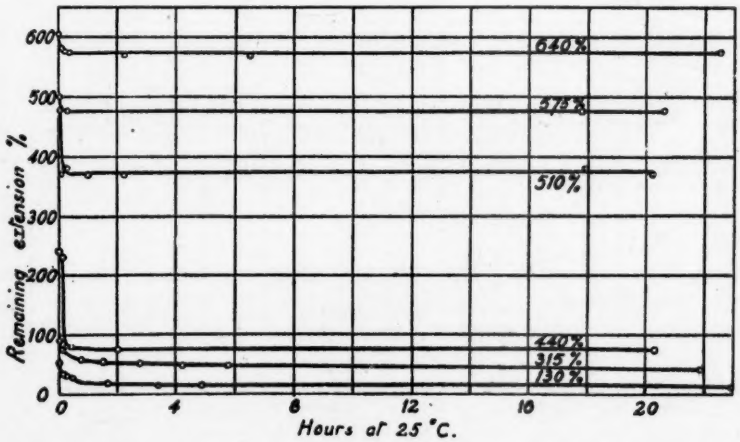

FIG. 4.—Recovery at 25° C after stretching 1 hour at 25° C. Elongations as marked.

tions there is no further recovery after the first half-hour, while for the lower elongations the recovery is more gradual, and also more complete.

Recovery at 25° C after Stretching at 50° C.—Similar data for samples stretched for 1 hour at 50° C are given in Figure 5. It will be observed that the gradualness of the recovery is more noticeable at this stretching temperature than at 25° C, and that the absence of gradual recovery is apparent only after relatively high initial elongations.

Recovery at Temperatures above 25° C.—Crystallization.—The recovery curves at 25° C thus fall into two main classes. In the first the recovery after releasing the tension is relatively small and ceases within about 30 minutes, while in the second the recovery is relatively large, and continues at a diminishing rate for at least 20 hours. The high extensions yield recovery curves of the first type, and the low extensions those of the second. Increase of stretching temperature favors the second type.

Two types of behavior are also observed when the recovery at higher temperatures is examined. There is the type of behavior represented in Figure 3, in which each increase in temperature gives a slight increase in the recovery; this type

of behavior corresponds with the lower degrees of extension. An entirely different type of behavior is depicted in Figure 6, which shows the effect of raising the temperature at the rate of about 1° C per 3 minutes. The specimens represented in this figure had been extended at 25° C for 1 hour, and subsequently allowed to recover for 20 hours at 25°. For the higher extensions practically the whole of the subsequent recovery occurred quite quickly over a temperature interval of only 1° C.

Similar experiments on specimens stretched at 50° C are more interesting because they show clearly the transition between the gradual and the critical-temperature types of recovery (Figure 7). For the highest extension, the temperature range over which most of the recovery occurred was as narrow as for a stretching temperature of 25°, but as the initial elongation was reduced the recovery range showed a corresponding broadening until, for an initial elongation of 480%, all signs of a special recovery temperature had disappeared.

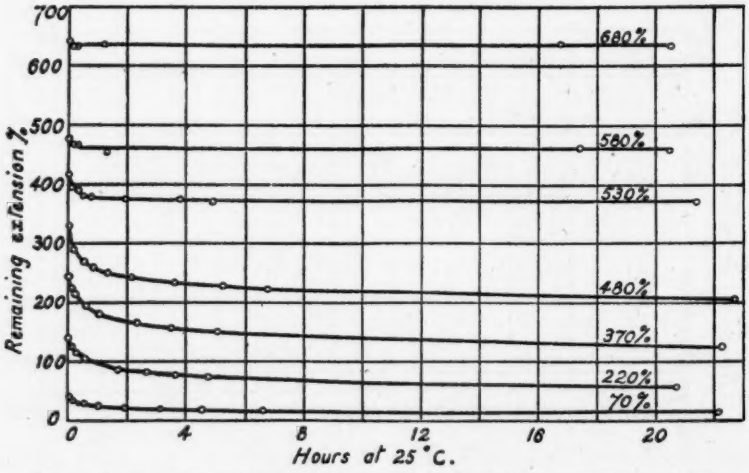

FIG. 5.—Recovery at 25° C after stretching 1 hour at 50° C. Elongations as marked.

These phenomena have been observed by a number of authors, in greater or less degree, and an explanation of the sharpness of the recovery temperature for highly extended rubber has been given by Feuchter and Hauser[6]. These workers found that on storing rubber "racked" to 600% extension the recovery range narrowed from 11° to 1°, and at the same time there was an increase in density of the rubber and an increase in the intensity of the x-ray "fibre" pattern. They concluded that these phenomena were associated with a high degree of crystallinity. On this view the recovery temperature is to be identified with the melting point of the crystals formed on stretching.

The data here brought forward generally tend to substantiate this view. It is to be expected, and it has been demonstrated by von Susich[7] from x-ray evidence, that the appearance of crystallization requires a higher degree of extension, the higher the temperature at which the extension is carried out. Hence the critical-temperature type of recovery would be expected to occur more readily at a lower than at a higher temperature, as is indeed found to be the case. There is, however, one feature of the experimental results for which no obvious explanation can be found, namely, that the recovery temperature depends on the

temperature at which the stretching is performed (*cf.* Figures 6 and 7). One would not expect the melting point of the crystals to depend on the temperature at which they were formed.

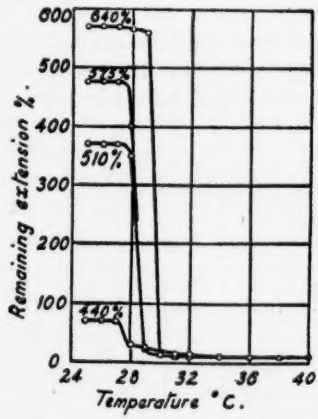

FIG. 6.—Recovery with rising temperature after stretching for 1 hour at 25° C to extensions indicated.

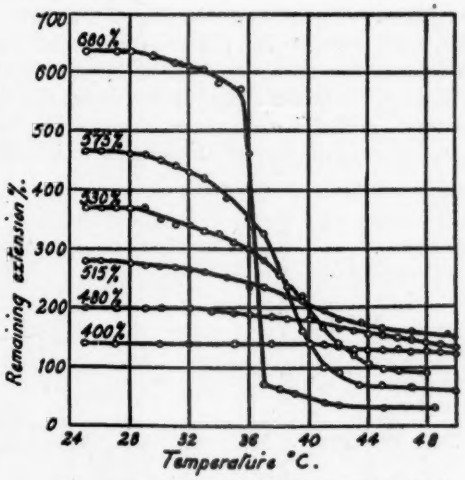

FIG. 7.—Recovery with rising temperature after stretching for 1 hour at 50° C to extensions indicated.

5. PLASTIC FLOW

After recovery at 25°, followed in some cases by further recovery at higher temperatures, the samples were treated by a benzene-alcohol mixture containing 50% of benzene for 16 hours, followed by a further treatment with a 60% benzene mixture for the same time. The extensions remaining after this treatment, representing plastic flow, are shown in Figure 8, for stretching temperatures of 25° and 50° C, respectively. A number of control specimens, not stretched, which were subjected to the same benzene-alcohol treatment, showed contractions ranging from 0 to 3%, which indicated that the original material was not in all cases perfectly free from strain, in spite of the precautions taken in its preparation. This effect accounts for the fact that in some cases the flow appeared to be negative. Although the accuracy was necessarily limited on this account, the general nature of the results cannot have been seriously affected, and the essential features of the data presented were repeated in a number of separate series of experiments. It is desired to draw attention especially to the following points:

1. The plastic flow increased to a maximum at intermediate extensions, and fell again at higher extensions.
2. The maximum flow on stretching at 25° C occurred at an elongation of about 300%, and amounted to only about 2% of the original extension.
3. For a stretching temperature of 25°, the flow was negligibly small for extensions exceeding 400%.
4. For a higher stretching temperature, *i. e.*, 50° C, the maximum flow occurred at a higher elongation, and the flow at any given elongation was higher.

If we accept the view that the total effect of cohesion between molecules in a crystalline lattice is greater than that between molecules in the disordered state,

the reduction of flow which occurred when a certain extension was exceeded may be explained as being due to the occurrence of crystallization. The fact that the maximum flow occurred at a higher elongation at the higher temperature would appear to be a direct result of the lesser degree of crystallinity at any given elongation. The general features of the flow phenomena are thus explicable on the same basis as the general features of the recovery phenomena dealt with in Section 4.

Whitby, from his experiments[4], drew the conclusion that the amount of flow increased with the elongation. However, he worked only up to 350% elongation, *i. e.*, on one side only of the maximum in the flow-elongation curve.

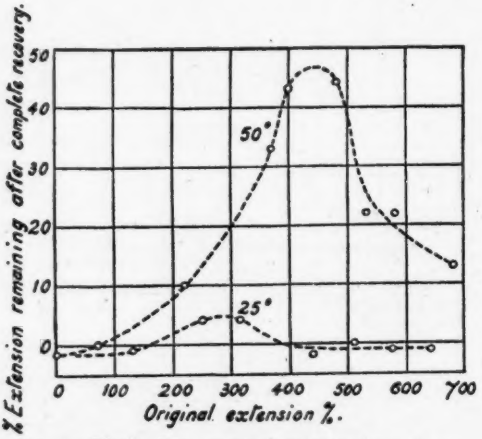

FIG. 8.—Plastic flow expressed as percentage of undeformed length for specimens held for 1 hour at various extensions at the temperatures indicated.

SOME CONSEQUENCES OF THE OBSERVED FLOW PHENOMENA

Besides being of interest from the theoretical point of view, the peculiar relation between plastic flow and initial elongation leads to certain considerations of practical importance. Since the flow is greatest at intermediate extensions, it is necessary that the intermediate region should be passed through as quickly as possible if the smaller flow characteristic of the higher elongations is to be observed. This is one of the reasons for the adoption, in the present work, of an automatic method of securing rapid extension of the rubber. Moreover, the effect undoubtedly has a bearing on the shape of the stress-strain curves obtained by Rosbaud and Schmid[2]. It accounts also for the observation of Hauser[8] that an x-ray fibre diagram could not be obtained when raw rubber was stretched very slowly, for in this case the region of maximum flow may never have been passed through and the molecular extension necessary for crystallization thus not achieved. Finally, it reveals the importance of making a careful study of the accompanying flow before attempting to discuss the meaning of the variations in the shape of stress-strain curves obtained at different temperatures and rates of elongation, and of the hysteresis observed in the stress-strain relationship. These effects are further complicated by the variation of tension with time, even when the flow is negligible. (See below.)

6. THE DECAY OF TENSION DURING EXTENSION

The change of tension with time, for specimens held at constant length, is shown in Figures 9 and 10. In plotting these curves the observed tensions have been converted to kg. per sq. cm. referred to the strain cross-section, assuming the density to remain unaltered by the extension. Two features of these curves call for special comment. First, for a given elongation the relative fall of tension is greater at the higher temperature, while at a given temperature it diminishes with increasing elongation. Secondly, the tension for a given elongation at 50° is in all cases very much lower than for the same elongation at 25°. This second result is not consistent with what is deduced from the simplest application of the statistical theory of rubber elasticity developed by Kuhn[9] among others, according to which the tension at constant elongation is directly proportional to

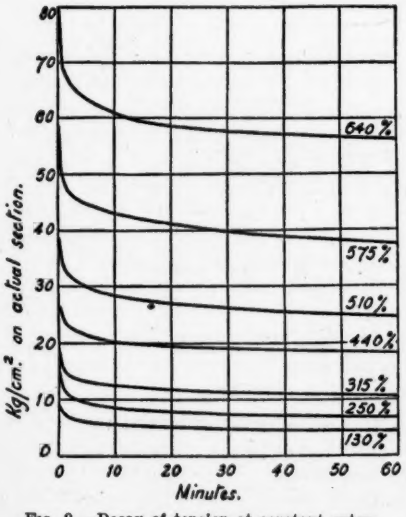

FIG. 9.—Decay of tension at constant extension at 25° C.

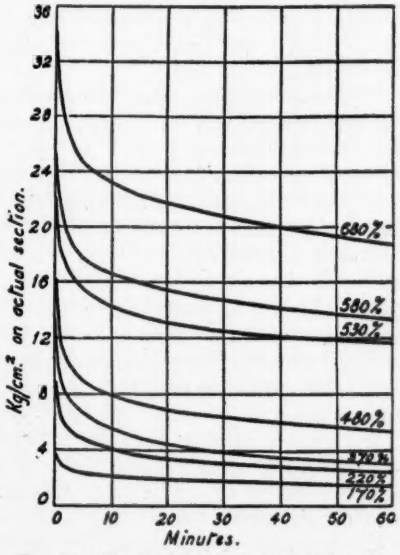

FIG. 10.—Decay of tension at constant extension at 50° C.

the absolute temperature. A linear rate of increase of tension with temperature has indeed been observed by Hauk and Neumann[10] for a number of vulcanized rubbers. The discrepancy cannot be disposed of by taking account of the plastic flow during stretching, this effect being much too small. A difficulty arises also in explaining the fall of tension at a fixed extension. For example, reference to Figures 8 and 9 shows that a fall of 30% may occur in the course of 1 hour for rubber elongated by 510% at 25°, though the flow under these conditions is negligible. How, then, is the fall to be explained?

7. THE STRUCTURE OF RAW RUBBER

As a basis for the present discussion the statistical theory of the behavior of single molecules developed by Kuhn[9] will be taken as fundamentally correct. According to this theory the essential elasticity of rubber is a property of the long-chain molecules of which it is composed. The tension exerted by an ex-

tended molecule represents the tendency for it to take up the statistically most probable overall length.

To account for the elastic properties of a solid, however, it is necessary to consider not only single molecules but also the aggregate of molecules and the forces between them. The molecules in unstretched rubber must be variously intertwined in an irregular manner. The process of extension, by which the molecules become straightened out, at least partially, and orientated in the direction of stretching, must therefore involve considerable relative displacements between adjacent portions of neighboring molecules, which the cohesional forces between them are not sufficient to prevent. In other words, the molecules can slide over each other with relative freedom. On the other hand, the fact that the flow is negligibly small at temperatures below 25° C proves that there must be present in the rubber a structure which remains unbroken during the deformation. Therefore, in spite of their relative mobility, the molecules of rubber must be held together at a sufficient number of points for this structure to be preserved. The experimental evidence thus leads directly to the following important conclusion:

The molecules of rubber are held together at certain points, or over certain regions, so as to form a three-dimensional structure. On deformation at a temperature not exceeding 25° C a sufficient number of these points of linkage or cohesion are maintained for this structure to remain substantially unchanged.

It is not suggested that the postulation of a structure of this kind to account for the behavior of elastic bodies is either new or original, but in view of the fact that raw rubber has been commonly regarded as being very imperfectly elastic, it does seem important that the above conclusion should be explicitly stated. By way of comparison, it is of interest to quote the conclusions arrived at by Busse[11] regarding the necessary conditions for the occurrence of high elasticity in general. These conditions are[12]:

1. "The presence of groups of atoms which form strong, somewhat flexible, fibrous units:

2. "weak or uniform cohesive forces around the fibres:

3. "an interlocking of the fibres at a few places along their length to form a 3-dimensional network. This interlocking may occur through chemical combination, by secondary valence forces, or by mechanical entanglement, and

4. "A means of storing up free energy in the fibres during deformation."

The Nature of the Cohesive Links between Molecules.—The results brought forward in this paper show that the links between the rubber molecules, *i. e.*, those referred to under Busse's 3rd condition, begin to break down at an appreciable rate at about 50° C. Therefore they cannot be primary chemical bonds. In this respect raw rubber differs from the vulcanized product, in which the bonds between molecules are of high energy. In raw rubber, the links (condition 3) may be due either to van der Waals' forces or to mechanical entanglements. Now we have seen that when fully extended, raw rubber crystallizes. In this case the forces holding the molecules in the crystalline lattice are undoubtedly of the van der Waals' type, for there are no others available. Yet, even in this very favorable case, in which the alignment increases the efficacy of the van der Waals' forces between molecules, the crystals are found to break down completely at a temperature in the neighborhood of 30° C. Such a mechanism cannot therefore of itself account for the persistence at higher temperatures of the links (condition 3) between molecules. It is necessary therefore to introduce Busse's suggestion, namely, the conception of mechanical entanglements, in conjunction with van der Waals' forces, to account for the observed properties. Such en-

tanglement-cohesions would possess a wide range of energies; hence at any stretching temperature some would break very much more quickly than others. Flow would occur when the number remaining unbroken fell below a certain value. There would appear to be a strong *a priori* probability of the formation of relatively stable linkages by mechanical entanglement if the view is accepted that the rubber molecules are very long (length/diameter > 1000), that they are arranged entirely at random with respect to each other, but are at the same time densely packed. Under such conditions two or more molecules might very well become twisted together or looped through each other in such a way that on the application of a shearing force a long time would elapse before separation occurred. Or, to put the matter in another way, the entanglements may be regarded as regions possessing an exceptionally high resistance to flow. If a number of such regions were interconnected by extensible (but unbreakable) molecules, the high viscosity characteristic of these regions would be retained as a property of the substance in bulk, while at the same time the general mobility of the individual molecules between the points of entanglement would remain.

A mechanism of this kind accounts qualitatively for a number of features of the mechanical behavior of raw rubber. Considering first the tension, we have to account for (*a*) a continuous fall of tension at constant length, without plastic flow, and (*b*) a lower tension after a given time at any extension at the higher temperature. With regard to (*a*), a fall of tension of the type shown in Figure 9 is just what would be expected from a series of links representing a wide range of binding energies. The low-energy links would break quickly, those of higher energy less quickly, and those of still higher energy, *i. e.*, involving considerable entanglement, very slowly or not at all. Consequently, the tension would fall rapidly at first, and thereafter more and more slowly. The same mechanism accounts for (*b*), for at a higher temperature all the links would break more quickly[13].

Consider now the recovery phenomena. During extension, simultaneously with the breaking of the original entanglement-cohesions between molecules, there will occur a formation of weaker entanglement-cohesions in the deformed state. The greater the degree of mechanical entanglement formed in the stretched condition, the greater will be the energy required to release the strain thus introduced. An increase of temperature will increase the possibility of the formation of new entanglement-cohesions, first because of the greater rate of release of the original linkages, and secondly because of the greater thermal agitation of the molecules. On the other hand, the emergence of a crystalline state will tend to reduce the formation of cohesions of the entanglement type.

These considerations lead to a fuller understanding of the recovery phenomena The new entanglements formed in the stretched condition, although of the same kind as those originally present in the unstretched rubber, will be less complex, and therefore more readily broken down. As with the original linkages, there will be a wide range of cohesional energies, but the average energy will be lower. Hence on releasing the applied tension the force of retraction resident in the individual molecules will cause the breaking down of the new rather than of the original entanglements. There will be a rapid reduction of length corresponding to the breaking of entanglements of low energy, followed by a progressively more and more gradual recovery, corresponding to the release of those of higher energy. An increase of temperature will clearly increase the rate of recovery, without altering its nature.

The theory, of course, accounts for the recovery phenomena only when crystallization is not present to an important extent, for under these circumstances,

as was pointed out above, the behavior is controlled by van der Waals' forces rather than by entanglement-cohesions.

SUMMARY

In considering existing information on the mechanical properties of raw rubber, it is not generally possible to distinguish between the effects of elastic and of plastic deformation. In the experiments described great care was taken to secure the complete removal of elastic strain, after stretching to various extensions at different temperatures. The plastic flow increased to a maximum with increasing elongation and fell again at higher elongations, an effect attributed to the increase of crystallization with increasing extension. For rubber held extended for one hour at 25° C the flow was never greater than 2% of the original extension, and for extensions greater than 440% or less than 130% it was negligibly small.

Curves showing the decay of tension at constant extension, and the recovery of length after stretching, in conjunction with the observations on plastic flow, are interpreted in terms of a theory proposed by Busse, according to which the rubber molecules are held together at certain points by cohesional linkages of low energy, some of which are broken down during stretching.

The author desires to express his indebtedness to Professor E. K. Rideal, who provided facilities at the Laboratory of Colloid Science, Cambridge, for carrying out part of this work, and also to J. K. Roberts of the same laboratory, who was responsible for directing the course of the research, and whose advice and criticism have proved invaluable.

The above work has been carried out as part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

REFERENCES

[1] A review of existing knowledge of the physical properties of raw rubber is to be found in Chapter II, by G. S. Whitby, in "The Chemistry and Technology of Rubber" (Reinhold Publishing Corp., New York, 1937).
[2] Rosbaud and Schmid, *Z. techn. Physik* **9**, 98 (1928).
[3] Feuchter, *Kautschuk* **2**, 260, 282 (1926).
[4] Whitby, *J. Phys. Chem.* **36**, 198 (1932).
[5] Staudinger, *Ann.* **488**, 127 (1931); *Ber.* **63**, 921 (1930).
[6] Feuchter and Hauser, *Kautschuk* **5**, 194, 218, 245, 276 (1929).
[7] von Susich, *Naturwissenschaften* **18**, 915 (1930).
[8] Hauser, *Kautschuk* **3**, 288 (1927); *Ind. Eng. Chem.* **19**, 169 (1927).
[9] Kuhn, *Kolloid-Z.* **76**, 258 (1936).
[10] Hauk and Neumann, *Z. physik. Chem.* **182A**, 285 (1938).
[11] Busse, *J. Phys. Chem.* **36**, 2862 (1932).
[12] See also "First Report on Viscosity and Plasticity", 2nd Ed., p. 98.
[13] For a discussion of the role of molecular entanglement in vulcanized rubber, the reader is referred to the work of Long, Singer and Davey (*Ind. Eng. Chem.* **26**, 543 (1934) on the time lag in the formation of the x-ray fibre pattern on stretching.

DIFFUSION OF SULFUR IN RUBBER

RELATION TO VULCANIZATION *

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A survey of the literature failed to disclose any previous attempt to determine the rate of diffusion of sulfur through rubber. The present paper is intended to fill this gap and to show the importance of diffusion and solubility of sulfur in rubber on control of the vulcanization reaction.

The vulcanization of rubber cannot be considered as a homogeneous chemical reaction since the reactants, *i. e.*, sulfur, accelerators and activators, are seldom completely in solution or uniformly dispersed. The limited solubility of sulfur, many accelerators, and zinc soaps in rubber leads to the presence of these substances partly in solution and partly in the dispersed state during vulcanization. Local high concentrations of these substances occur in solution around the dispersed phase, owing to their increased solubility which results from the temperature rise during vulcanization, coupled with their slow rate of diffusion through rubber.

This paper presents the results of a detailed study of the effects of solubility, diffusion, and crystallization of sulfur on heterogeneity of vulcanization. Results showing the effect of various methods of mixing and handling on the physical properties of certain rubber compounds are presented.

The diffusion of sulfur into rubber to form a solution during vulcanization, followed by the separation of globular sulfur on cooling, and its transition into dendritic and finally into rhombic sulfur on standing, was observed under the microscope by Loewen[9, 10] and Endres[3]. Several factors which influence the migration and crystallization of sulfur internally and as a surface bloom on rubber were studied by Rimpel[13], Endres[3, 4], Twiss[20], Loewen[10], and Graffe[5].

The absorption of sulfur by rubber at elevated temperatures was studied by Skellon[17] and by Venable and Green[21], and the solubility of sulfur at various temperatures was investigated by Venable and Green[21], Endres[3], Kelly and Ayers[7], Loewen[10], Morris[11], and Williams[23].

ABSORPTION OF SULFUR BY RUBBER

Venable and Green[21] studied the absorption of sulfur by sheets of rubber embedded in powdered sulfur at various temperatures to determine the solubility of sulfur in rubber. It was assumed in this work that the rubber would absorb sulfur until saturation was established and then stop. Since this work was of a preliminary character and quite inconclusive, the present authors deemed it advisable to repeat it.

The procedure used in the present investigation was to place thin sheets of rubber, 3.8 cm. square, in a powdered sulfur pack and heat for various periods at a controlled temperature. Following each period of heating, the sheet was removed and cooled, and the sulfur was brushed off uniformly with a camel's-hair brush. The sheet was weighed after each period of heating to determine the increase in weight resulting from the absorption of sulfur. The amount of adhering

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sulfur was found to be fairly constant and was determined initially in order to make a correction for it in subsequent weighings. Typical data for this type of experiment are given in Table I, which shows the sulfur absorption of molded sheets of masticated crepe rubber after various periods of heating at 56° C in a pack powdered sulfur.

Examination of these data indicated that equilibrium is not reached even after heating for 3215 hours. Since the amount of sulfur absorbed greatly exceeded the known solubility of sulfur in rubber, internal crystallization was suspected. Microscopic examination showed the presence of a large quantity of crystalline sulfur in the rubber at the end of the long heating period.

The absorption data are plotted logarithmically in the upper part of Figure 1, along with those obtained in similar experiments where temperature and sheet thickness were varied. Following an initial period of higher absorption rate, all of the results fall on a straight line, with slopes varying from 0.20 to 0.22.

When the sulfur absorption values for masticated crepe determined at various temperatures are plotted against the fifth root of time, as in the lower part of Figure 1, straight lines result, which pass through the origin. The slope is increased by increased temperature and decreased by increased thickness of the rubber sheet, as would be expected. Although the earlier values up to 21 hours given in Table I are lower than is indicated by curve 2 in the lower part of

TABLE I

ABSORPTION OF SULFUR BY MASTICATED CREPE AT 56° C

Heating period (Hrs.)	% weight gain [a]			Heating period (Hrs.)	% weight gain [a]		
	I	II	III		I	II	III
0.5	0.43	0.78	0.63	49	6.10	6.48	6.10
1.5	1.49	1.49	1.56	90	6.84	7.16	6.73
3	2.22	2.31	2.42	165	7.70	8.03	7.61
5	2.86	2.92	3.08	263	8.48	8.73	8.34
7	3.35	3.55	3.55	352	9.26	9.44	9.00
9	3.76	3.91	3.90	495	9.84	10.09	9.54
11	4.03	4.26	4.10	687.5	10.52	10.67	10.25
13	4.30	4.53	4.34	763.75	10.87	10.98	10.69
15	4.50	4.78	4.57	1340	11.80	11.96	11.55
21	4.81	5.08	4.90	2078	12.83	13.08	12.57
27	5.26	5.60	5.25	2562	13.94	14.03	13.76
43	5.72	6.10	5.80	3215	14.95	15.08	14.72

[a] Samples had the following properties:

Sample No.	Weight (Gram)	Thickness (Cm.)	Initial Adhering S (Gram)
I	0.8213	0.0584	0.0430
II	0.8464	0.0610	0.0432
III	0.8662	0.0635	0.0440

Figure 1, the one-hour absorption values must be taken from the plotted straight lines if they are used to calculate absorption values for longer periods using the following formula:

$$C = C_1 \sqrt[5]{t}$$

where C_1 = absorption in some unit time such as 1 hour or 1 day. Taylor and Kemp[19] found the following relation to hold for water absorption by rubber:

$$C = C_1 \sqrt[2]{t}$$

To determine the effect of long time absorption without frequent removal and weighing, a specimen of masticated crepe, 0.053 cm. thick, was placed in a sulfur

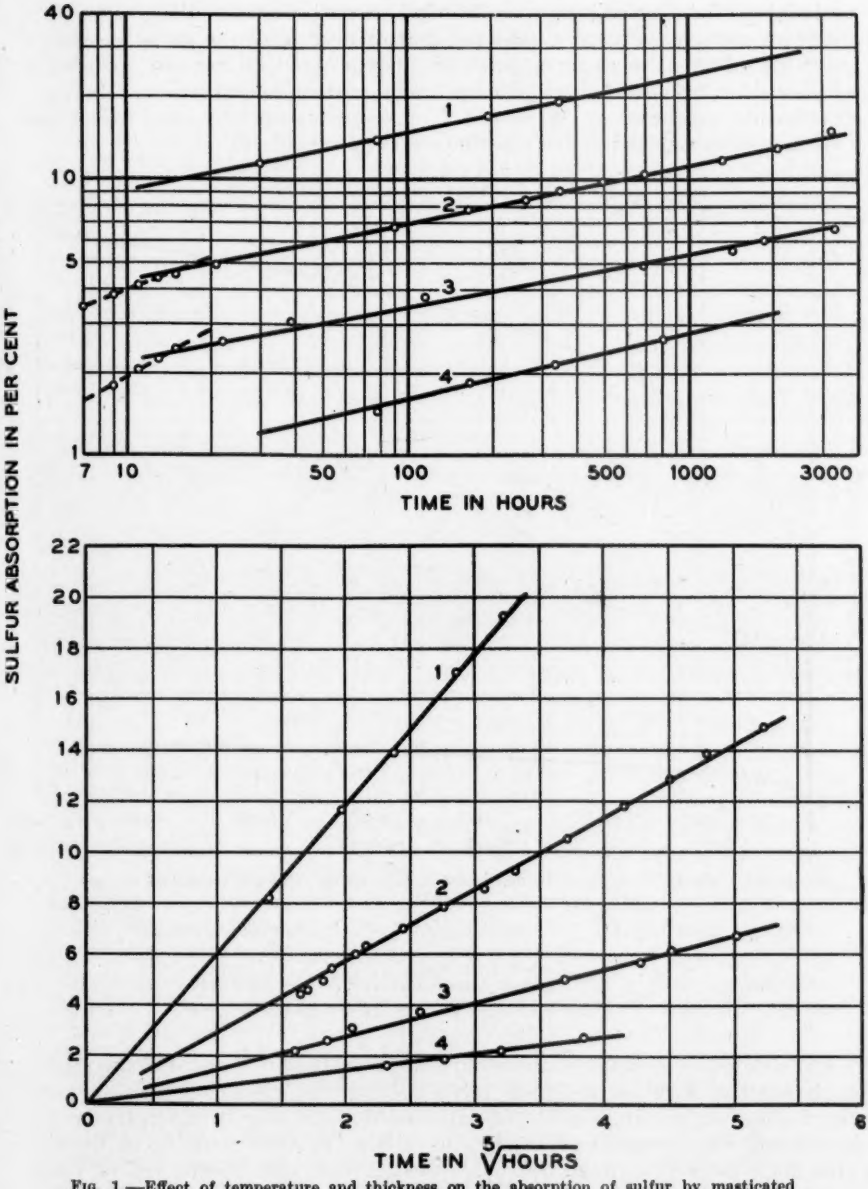


FIG. 1.—Effect of temperature and thickness on the absorption of sulfur by masticated crepe rubber.

Curve No.	Temp., ° C	Thickness, Cm.
1	86	0.0584
2	56	0.0610
3	56	0.203
4	25	0.0572

pack for 3000 hours and kept undisturbed at 25° ± 0.3° C. When weighed it showed a sulfur absorption of 2.88 per cent or over twice the sulfur saturation value for rubber at this temperature. Fluctuating temperatures and disturbance of the rubber would be expected to promote internal crystallization. However, experiments conducted at 56° ± 0.05° C gave practically the same absorption values as were obtained in the experiments already recorded.

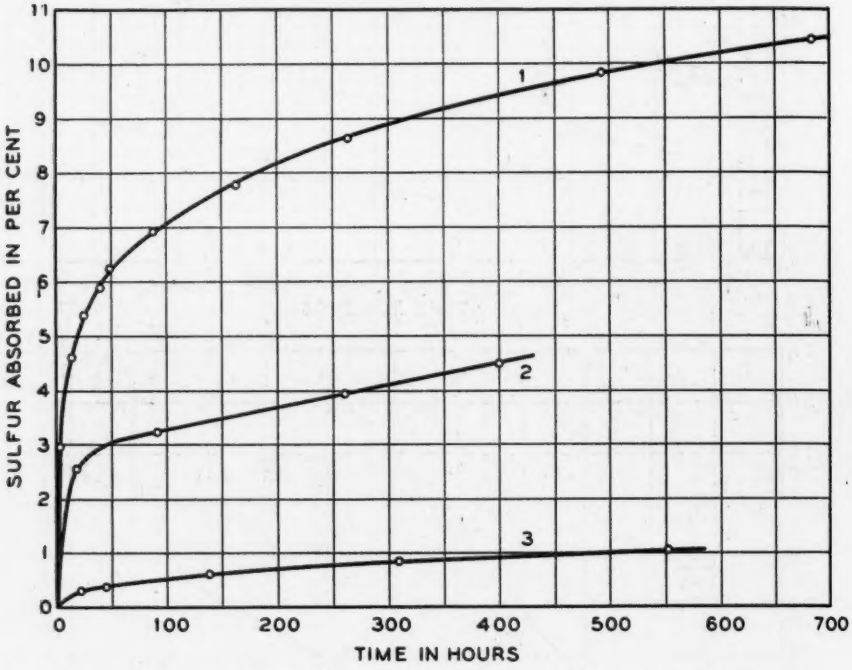


FIG. 2.—Absorption of sulfur by masticated crepe, latex gel, and soft vulcanized rubber at 56° C.

Curve No.	Rubber	Thickness (Cm.)
1	Masticated crepe	0.0610
2	Washed latex film	0.0457
3	Soft vulcanized [a]	0.0559

[a] 95 crepe + 5 sulfur, vulcanized 4 hours at 141° C. (2.85% combined sulfur.)

The absorption of sulfur by rubber appears to be osmotic in nature, and similar to the swelling of rubber in organic solvents. Since the rubber swells in the process of absorbing sulfur, it might be expected that the rate of absorption would be reduced with increased stiffness of the rubber. This was found to be the case with latex gel hydrocarbon, soft vulcanized rubber, and ebonite, all of which show a lower rate of absorption than masticated crepe. Sulfur absorption data on masticated crepe, gel hydrocarbon, and soft vulcanized rubber are compared in Figure 2. The absorption of sulfur at 86° C by an ebonite sheet 0.08 cm. in thickness was found to be less than 0.2 per cent after heating in a sulfur pack for 670 hours. This would indicate either a low rate of diffusion or a low solubility of sulfur in ebonite, or both, since the solubility value should be exceeded in this period. It is probable that the high resistance of ebonite to

swelling accounts for its low sulfur absorption. The same explanation has been given for the low water absorption of ebonite[25]. No reliable data are available on the solubility of sulfur in ebonite, although it has been assumed by some to be high because blooming of sulfur does not take place when a high content of free sulfur is present.

The conclusion to be drawn from this work is that the determination of the absorption of sulfur by rubber in contact with it is not a satisfactory method to establish the solubility of sulfur in rubber when employing the present technique.

RATE OF DIFFUSION OF SULFUR INTO RUBBER

An experiment was devised to determine the rate of diffusion of sulfur into a one-inch cube of plastic crepe rubber. Crepe rubber was milled 10 minutes and molded in a cubical aluminum mold with cellophane films on each face as shown in Figure 3. One face of the mold and cellophane were removed, and sulfur

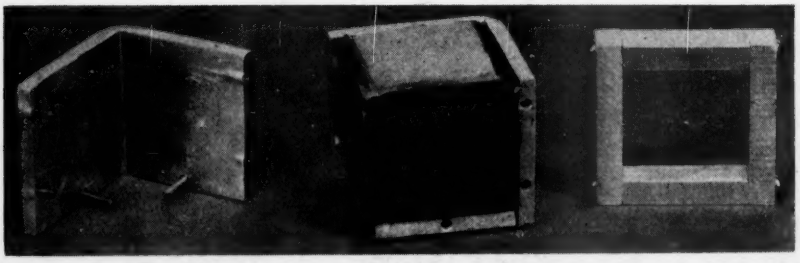


FIG. 3.—Mold for sulfur absorption experiment with cube of rubber.

was packed against this face, while the other sides of the cube were protected against contact with the sulfur. In one experiment this assembly was heated for 500 hours at 56° C, and in another identical experiment the heating was continued for 1000 hours. At the end of these heating periods the external sulfur was removed, and the cube taken from the mold and cut into four approximately equal sections. The total sulfur was determined in each segment. The face of the section contacting the sulfur was brushed to remove loosely adhering sulfur, and this surface-adhering sulfur was corrected for as described previously. The data showing the average sulfur content of each segment in these experiments are plotted in Figure 4, and show the distribution of sulfur through the rubber at the end of 500 and 1000 hours of heating at 56° C.

Curve 1, Figure 4, gives approximately the concentration of sulfur in an inch-thick slab of masticated crepe rubber under conditions of sulfur diffusion equilibrium at 56° C, where the vapor pressure of sulfur on the side opposite the sulfur is kept at zero. Curve 2 shows the result of considerable sulfur accumulation following the establishment of the diffusion equilibrium gradient. From the extrapolation of curve 1, the sulfur wave front is found to pass through masticated crepe rubber at a rate of about 0.0056 cm. per hour at 56° C.

RATE OF SULFUR DIFFUSION THROUGH RUBBER

To measure the rate of sulfur diffusion through rubber accurately, a diffusion cell placed in a gastight container as shown in Figure 5 was constructed. This

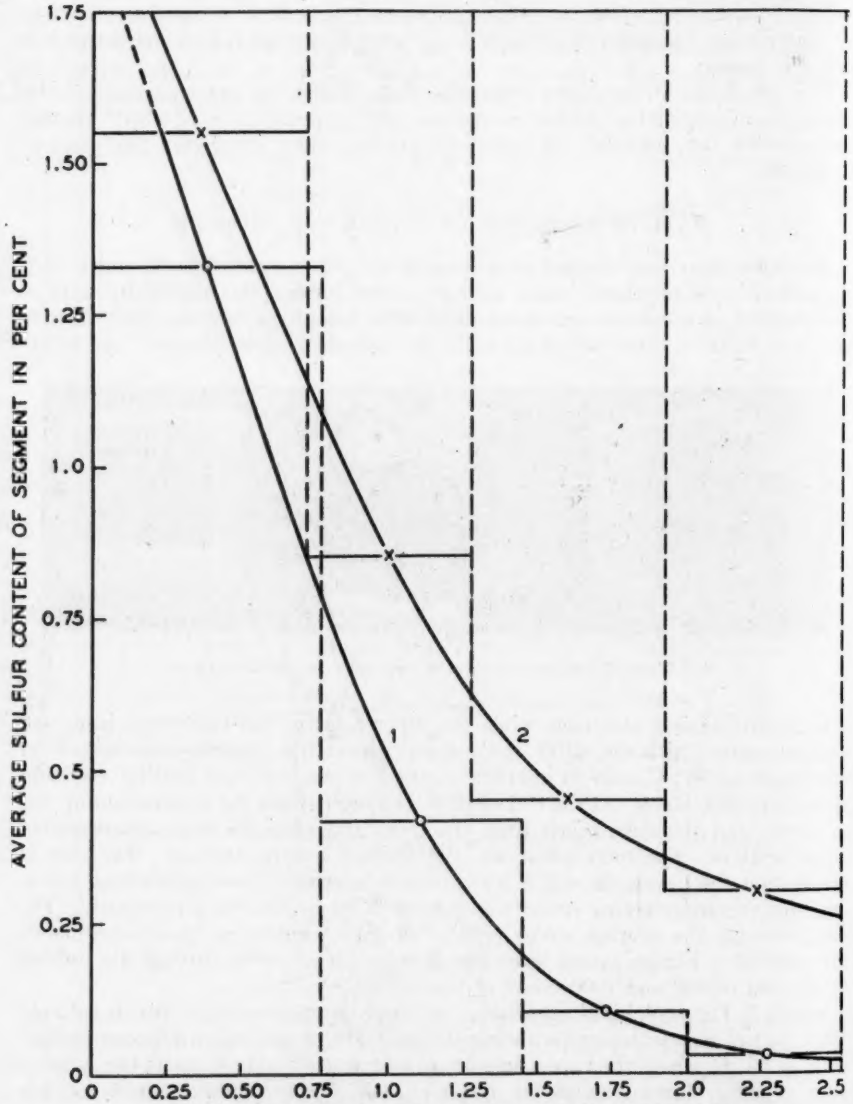


FIG. 4.—Concentration gradient of sulfur in cube of masticated crepe rubber resulting from sulfur diffusion.

1. After heating 500 hours at 56° C.
2. After heating 1000 hours at 56° C.

cell and container were placed in a specially constructed air oven held to a temperature which fluctuated ±0.2° C within the cell. Nitrogen was passed at about 20 liters per hour through a preheating coil and then through the container to remove the sulfur vapor as soon as it came through the upper surface of the rubber, as shown in Figure 6. The diffusion cell was removed, cooled in a desiccator, and weighed periodically. The loss in weight after diffusion equilibrium is reached was taken as a measure of the rate of diffusion of sulfur through

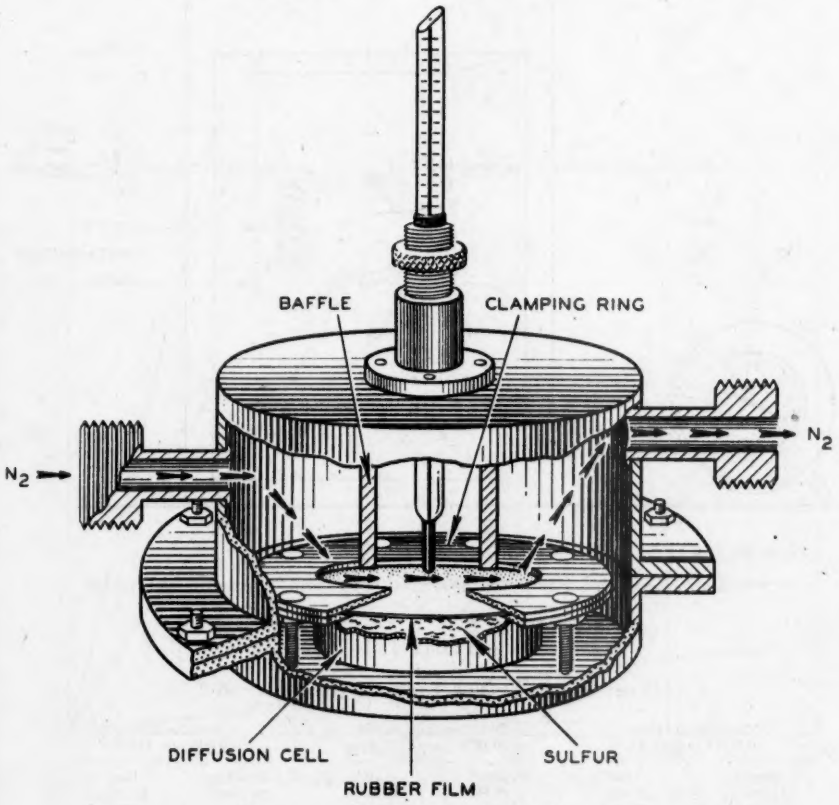


FIG. 5.—Apparatus for determination of sulfur diffusion through rubber.

the rubber. The sulfur was rubber-maker's grade sieved through a 60-mesh screen and dried over P_2O_5 before being placed in the cell. The cell was filled with the sulfur so that the bottom surface of the rubber rested on it. The data for the diffusion of sulfur through masticated crepe and soft vulcanized rubber at various temperatures are plotted in Figure 7. These data show that the rate of diffusion through masticated crepe at 86° C is somewhat higher than through vulcanized rubber. The diffusion rate through masticated crepe appears to decrease after long heating, which indicates that some vulcanization is taking place which reduces the rate to that of soft vulcanized rubber. Owing to the fact that the free sulfur in the outer surface layer of the vulcanized rubber would be

evaporated during the early heating period, the initial loss in weight is increased, as indicated in Figure 7, where the extrapolation of curve 3 crosses above the zero point. The diffusion of sulfur through a sheet of ebonite was determined at 86° C. The rates of sulfur diffusion through these materials are shown in Table II.

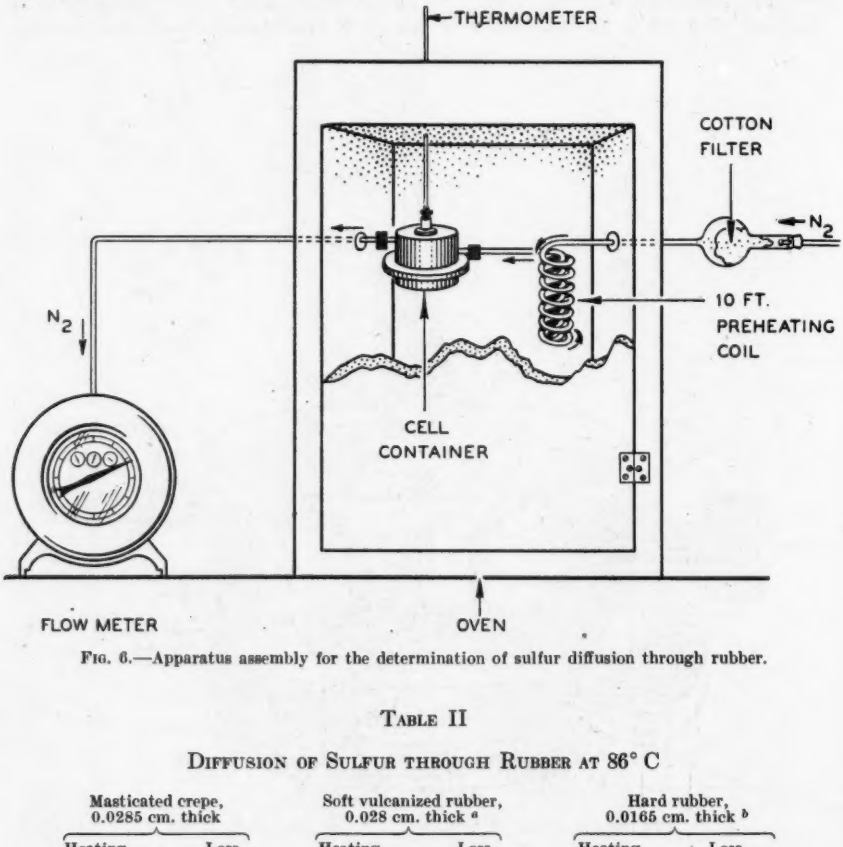


FIG. 6.—Apparatus assembly for the determination of sulfur diffusion through rubber.

TABLE II

DIFFUSION OF SULFUR THROUGH RUBBER AT 86° C

Masticated crepe, 0.0285 cm. thick		Soft vulcanized rubber, 0.028 cm. thick [a]		Hard rubber, 0.0165 cm. thick [b]	
Heating period, hr.	Loss in wt., gram	Heating period, hr.	Loss in wt., gram	Heating period, hr.	Loss in wt., gram
44	0.0072	46	0.0071	25	0.0006
25	0.0038	43	0.0055	22.5	0.0002
67	0.0109	72	0.0086	23.5	0.0001
44	0.0070	45	0.0053	70	0.0000
44	0.0061	44	0.0059	91	0.0002 gain
67	0.0090	71	0.0085		

[a] Composition given in Table III.
[b] Crepe rubber 73.00 + sulfur 27.00, vulcanized 10 hours between tin sheets at 149° C.

The first loss in weight of the ebonite appeared to be due to volatile matter held in the material, following which practically no sulfur diffused through the sheet within the limit of accuracy of weighing the cell. This zero order of sulfur diffusion rate through hard rubber explains the absence of blooming from ebo-

nite which contains high contents of free sulfur after cure. It would appear that the molecular structure of ebonite is such that the intermolecular spaces are smaller than the size of the sulfur vapor particles.

It is desirable, in comparing diffusion rates, to calculate the diffusion constant or specific diffusion rate according to Ficks' law, as done by Taylor, Herrmann, and Kemp[18] in the case of moisture diffusion through rubber. To do this it is

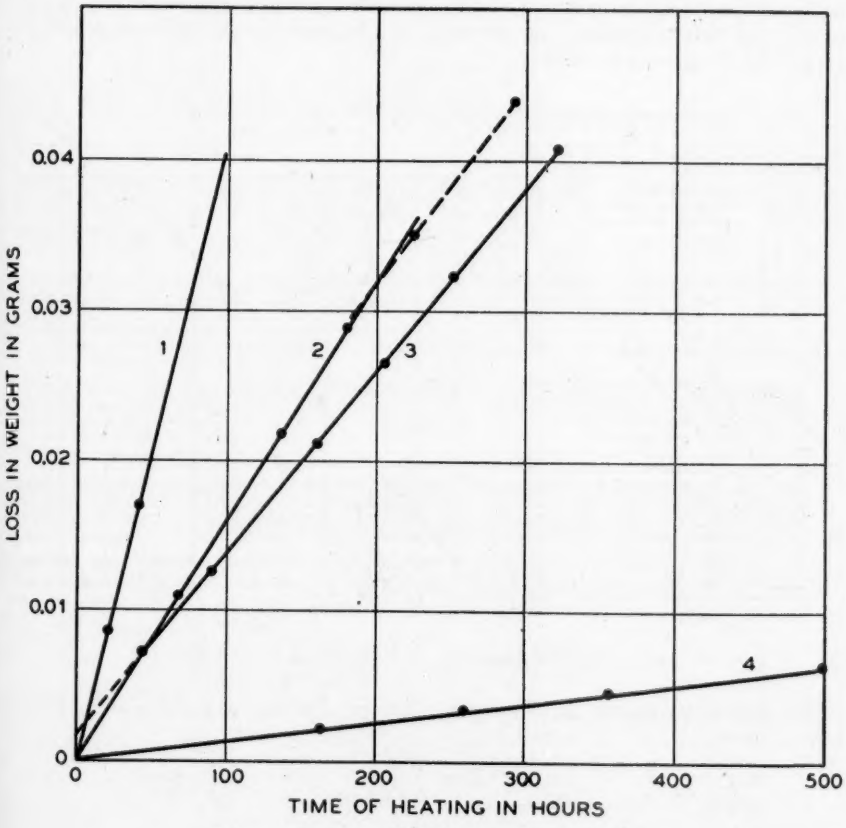


FIG. 7.—Rate of diffusion of sulfur through rubber.

Curve No.	Rubber	Thickness (Cm.)	Temp., ° C.
1	Masticated crepe	0.0305	96
2	Masticated crepe	0.0305	86
3	Soft vulcanized	0.0279	86
4	Masticated crepe	0.0279	58

necessary to know the vapor pressure of sulfur at the temperature employed. Since the values given by the International Critical Tables did not appear to represent a satisfactory analysis of the published work, a careful study was made of the methods used and results obtained by various investigators of the subject. These values, plotted in Figure 8, show a wide discrepancy.

The most extensive and careful work appears to have been carried out by Gruener[6]. In Figure 8, Gruener's results are plotted, with the mean results

taken from the voluminous literature on the vapor pressure of sulfur above 120° C, as given in the International Critical Tables. The plot of Gruener's results crosses those for higher temperatures, the extrapolation of which has a somewhat lower slope. Since transitions in sulfur occur at 95.5°, 112.8°, 119°, and 160° C, the extrapolation from the values at higher temperatures to those at lower temperatures is not entirely warranted. The results of West and Menzies[22] agree well with those of Gruener, but those of Neumann[12] and of Ruff and Graf[14] are entirely out of line, as is the one result of Brown and Muir[2]. In view of this discussion, the selection of Gruener's results for temperatures up to 120° C appears justified.

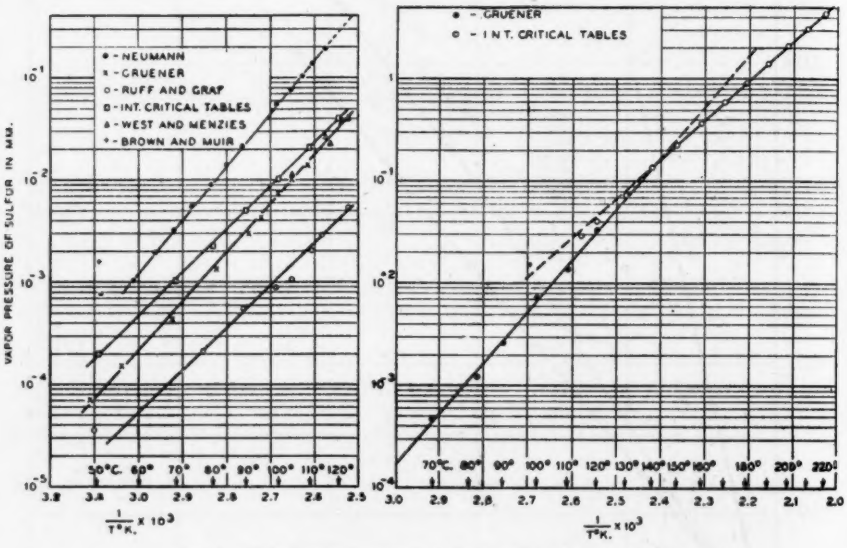

• - NEUMANN
x - GRUENER
o - RUFF AND GRAF
□ - INT. CRITICAL TABLES
Δ - WEST AND MENZIES
+ - BROWN AND MUIR
VAPOR PRESSURE OF SULFUR IN MM.
50°C. 60° 70° 80° 90° 100° 110° 120°
3.8 3.4 3.0 2.9 2.8 2.7 2.6 2.5
1/T°K. x 10³
• - GRUENER
o - INT. CRITICAL TABLES
70°C. 80° 90° 100° 110° 120° 130° 140° 150° 160° 180° 200° 220°
3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0
1/T°K. x 10³

FIG. 8.—Effect of temperature on the vapor pressure of sulfur.

The diffusion constant D or specific diffusion rate was calculated from Ficks' law; *i. e.*:

$$D = \frac{N x}{A t p}$$

where N = weight of sulfur lost (grams)
x = thickness of rubber sheet (cm.)
A = area of rubber exposed to diffusion (sq. cm.)
t = time of diffusion (hours)
p = vapor pressure of sulfur (mm.)

The calculated diffusion constants are given in Table III, and show that the specific rate of diffusion of sulfur through masticated crepe is slightly higher than it is through soft vulcanized rubber, and that the rate increases with temperature, as would be expected.

Although the diffusion constant for sulfur through rubber at 86° C is much higher than for water through rubber at 25° or 35°, the actual diffusion rate of sulfur is much less because of its lower vapor pressure. If the cell were filled with moisture under the same conditions given in Table II, it is calculated that

moisture would pass through a film of soft vulcanized rubber at a rate of 0.0069 gram per hour, or about fifty-five times as fast as sulfur at 86° C. This calculation neglects any change in the diffusion constant of water through rubber by increasing the temperature from 35° to 86° C. Since the diffusion constant increases with temperature, this difference should actually be greater.

Schumacher and Ferguson[16], and Sager and Sucher[15], found that moderate amounts of compounding ingredients did not affect the diffusion of moisture or of gases through rubber. The same conclusion probably applies in the case of

TABLE III

CALCULATED SULFUR DIFFUSION CONSTANT FOR RUBBER

	Temp. (° C)	Sheet thickness (Cm.)	Av. weight loss (G. per hr.)	Area of cell (Sq. cm.)	Vapor pressure of S [a] (Mm. Hg)	Diffusion Constant D (G. per hr. per cm. per mm. Hg)
Masticated crepe	58	0.0279	0.0000126	5.06	1.7×10^{-4}	4.1×10^{-4}
	86	0.0305	0.000160	5.06	2.2×10^{-3}	4.4×10^{-4}
	96	0.0305	0.000422	5.06	4.7×10^{-3}	5.4×10^{-4}
Soft vulcanized rubber[b].	86	0.0279	0.000124	5.06	2.2×10^{-3}	3.1×10^{-4}

[a] From Gruener's results in Figure 8 (lower).
[b] Crepe rubber, 100.0; zinc oxide, 6.0; sulfur, 3.0; stearic acid, 1.0; Altax (benzothiazyl disulfide), 1.0. Vulcanized 60 minutes at 135° C.

TABLE IV

PERMEABILITY OF SULFUR, HYDROGEN, AND MOISTURE THROUGH SOFT VULCANIZED RUBBER

(Sheet thickness 0.03 cm., temperature 58° C)

Vapor pressure (Mm.)	Permeability (G. per sq. m. per 24 hrs.)	Permeability (Moles per sq. m. per 24 hrs.)	Ratio to Permeability of S (Moles per sq. m. per 24 hrs.)
Sulfur			
1.7×10^{-4}	0.56	0.0022	1.0
1.0	3300	13	1.0
Hydrogen			
760	2.86	1.43	650
1	0.0038	0.0019	0.00015
Moisture			
135.6	115	6.4	2900
1.0	0.85	0.047	0.0036

the diffusion of sulfur through rubber; however, experiments were not conducted to prove this point.

From Sager and Sucher's results the permeability of hydrogen at atmospheric pressure and 58° C through a rubber sheet 0.03 cm. thick is taken as 32 liters, or 2.86 grams per square meter, in 24 hours. According to the data in Table III, sulfur at 58° C would pass through a sheet 0.03 cm. thick at a rate of 0.56 gram per square meter per 24 hours. From the results of Taylor, Herrmann, and Kemp[18] moisture at 58° C or at a vapor pressure of 135.6 cm. would pass through a 0.03-cm. sheet of rubber at a rate of 115 grams per square meter per 24 hours. Some values have been calculated which show the relative rates of diffusion of hydrogen, sulfur, and moisture through a 0.03-cm. thick sheet of soft vulcanized rubber at 58° C. These results in Table IV show that, under the

vapor pressure existing at 58° C, the molecular diffusion of hydrogen is 650 times that of sulfur, but that under 1 mm. vapor-pressure difference, sulfur diffuses 6700 times faster than hydrogen.

SOLUBILITY OF SULFUR IN RUBBER

The data in the literature on the solubility of sulfur in rubber are plotted in Figure 9 and show a considerable difference between the values given by Loewen[10], by Morris[11] and by Williams[24]. The values of Kelly and Ayers fall

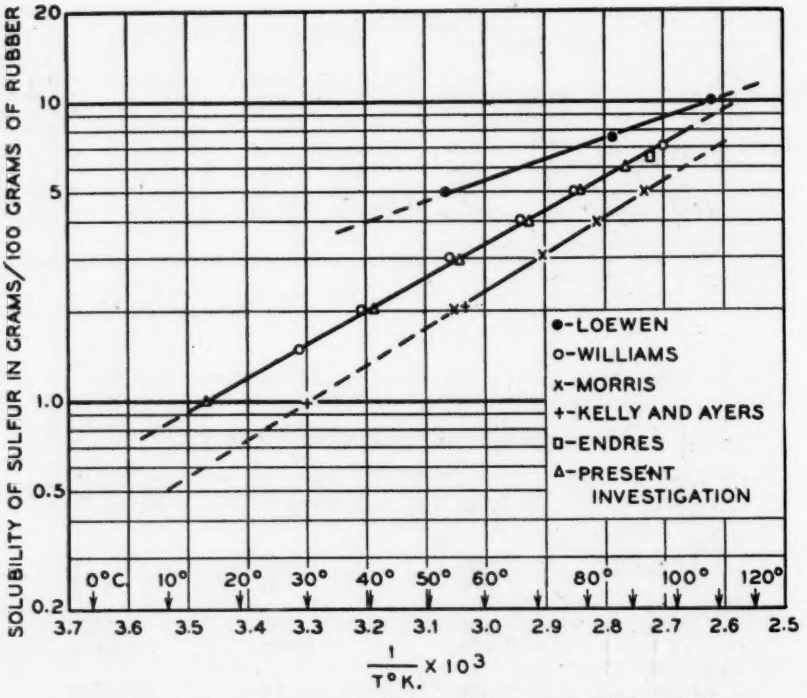


FIG. 9.—Effect of temperature on the solubility of sulfur in masticated crepe rubber.

on the same straight line as those of Morris, and one value at 95° C reported by Endres[3] falls close to Williams' results.

In view of the large differences in the results obtained by the different investigators, it seemed important to determine which values were most reliable. Crepe rubber was mixed on a mill with sulfur varying in amount from 1 to 5 parts per 100 parts of rubber in steps of 1 part for a period sufficient to dissolve all of the sulfur, judged by microscopic examination. When these mixtures were allowed to stand at room temperature, the one containing 1 part of sulfur did not show sulfur precipitation after standing for several weeks at 20° C, whereas the one containing 2 parts of sulfur showed the first separation of dendritic sulfur after standing in slab form for 48 hours at room temperature after milling. The sulfur in the mixture containing 3 parts of sulfur precipitated after 30 minutes, but those with higher contents became cloudy almost immediately. Mixtures

containing 1 and 2 parts of sulfur were placed overnight in a refrigerator at 6° C, which resulted in the separation of considerable sulfur in the specimen containing 2 parts. The specimen with 1 part of sulfur showed the separation of a small quantity of sulfur and became slightly cloudy. The temperature of this sheet was gradually raised until it became clear, which indicated that the sulfur was dissolved. It was then slowly cooled to 12° C, whereupon unmistakable separation of sulfur occurred. Repeating these observations, it was estimated that 1 part of sulfur is soluble in rubber at 14° C. Figure 9 shows that this result falls on the extrapolated line connecting Williams' results.

Sheets containing 2 parts of sulfur were placed in an air oven with a glass door through which changes could be observed microscopically. Specimens were placed in an oven at 40° ±0.5° C (*a*) immediately after milling; (*b*) after standing 48 hours at room temperature, during which period the separation of sulfur occurred, and (*c*) after overnight storage in a refrigerator at 6° C. No separation of sulfur occurred in specimen *a* after 5 days. A large part of the dendritic sulfur

TABLE V

SOLUBILITY OF SULFUR IN MASTICATED CREPE RUBBER AT VARIOUS TEMPERATURES

Temp. detd. experimentally (° C)	Temp. from plot in Fig. 9 (° C)	Solubility (G. per 100 g. rubber)
14 [a]	15	1.0
40 [a]	40	2.0
55 [b]	56	3.0
70 [b]	70	4.0
78.5 [b]	79	5.0
88 [b]	88	6.0
—	96	7.0
—	103	8.0
—	110	9.0
—	116	10.0

[a] Obtained by slow cooling to determine cloud point.
[b] Obtained by milling experiments.

which had separated in specimen *c* transformed into rhombic crystals, some of which were grouped in long chains. In the case of specimen (*b*), the small quantity of sulfur which had separated did not redissolve completely until the temperature was raised several degrees. When the temperature was lowered to 38° C, unmistakable separation of sulfur occurred in specimen *a* after standing overnight. These observations led to the conclusion that 2 parts of sulfur saturate 100 parts of masticated crepe rubber at 40° C.

To determine the temperature of saturation of 3, 4, 5, and 6 parts of sulfur in rubber, careful observations were made during milling to determine the lowest temperature required for complete solution. When the sulfur was in complete solution, the temperature was gradually lowered to determine the cloudy point and then raised to determine the clear point. Supersaturation effects were practically eliminated by the milling, and it was possible to ascertain the point of sulfur separation within ±1° C, after acquiring the technique. The values obtained in this investigation are given in Table V, and are compared with those taken from the plot of Williams' results in Figure 9.

After considerable undissolved sulfur has separated from rubber, one expects this sulfur to go into solution slowly when the mixture is heated at its saturation temperature, because sulfur diffusion is extremely slow with the low concentra-

tion gradient existing between the sulfur and the rubber adjacent to it. To cause this sulfur to dissolve in a reasonable length of time, the temperature must be raised considerably to increase the solution gradient. This technique leads to saturation temperatures which are too high, as indicated by the work of Morris[11]. If the temperature of a mixture containing all the sulfur in solution is lowered too rapidly, supersaturation occurs, and low results for saturation temperature will result, as pointed out by Williams. Loewen's results appear to have been obtained in this manner. The technique employed by Williams avoided the above difficulties. Determination of solubility on the mill also made it impossible to obtain supersaturation, since the rubber was being actively mixed during heating and cooling. Gradual cooling with disturbance of the sample to determine the first indication of cloudiness leads to satisfactory results.

In view of these considerations and the fact that our results are in close agreement with those of Williams, the straight line connecting Williams' results[25] and our results shown in Figure 9, is believed to be most acceptable.

RATE OF SOLUTION OF SULFUR DURING MILLING

To determine the approximate time necessary for sulfur to dissolve during milling, the following procedure was used:

1. Initial roll temperature, 66° C.
2. Breakdown, 400 grams crepe rubber, 10 minutes, with mill rolls opened to 0.038 cm. for first 3 minutes, and 0.14 cm. for next 7 minutes.

TABLE VI

MILLING TIME NECESSARY FOR COMPLETE SOLUTION OF SULFUR IN CREPE RUBBER

Parts S added per 100 parts rubber	Temp. of batch during milling (° C)	Time for complete solution of S (Min.)
1	72 ± 1	4
2	72 ± 1	6
3	78 ± 2	12
4	73 ± 2	16
5	80 ± 2	32
5.5	80 ± 2	55[a]

[a] Cloudiness at end of this period showed that the solubility of sulfur in rubber is exceeded.

3. Batch cut at 30-second intervals.
4. Rolls opened to 0.20 cm. after 10-minute breakdown.
5. Sulfur added in next 2 minutes. The sulfur used was screen-tested, and 91 per cent was found to pass through a 120-mesh sieve, 72 per cent through 200 mesh, and 45 per cent through 325 mesh.

Immediately after the addition of the sulfur, and at 2-minute intervals thereafter, microscopic observations were made on specimens taken from the mill rolls to note the point of complete solution. The data obtained are given in Table VI. These results show that the time required for complete solution of sulfur in rubber at normal milling temperatures depends on the amount of sulfur added. This time increases considerably when the sulfur content approaches the saturation value at the milling temperature employed. Higher milling temperatures would obviously reduce the time necessary for solution, and increase the limiting amount of sulfur which can be dissolved on the mill.

HETEROGENEOUS OR SPOTTY VULCANIZATION

Several years ago heterogeneous or spotty vulcanization was noted in the case of certain pure gum stocks which were vulcanized with 2.5 per cent of sulfur, using either tetramethylthiuram monosulfide or mercaptobenzothiazole acceleration. Recent investigation has shown that this condition is caused by the presence of undissolved sulfur in the rubber at the start of vulcanization. Standard practice calls for allowing the mixed and sheeted stock to stand 24 hours at room temperature before cure. If sulfur has been dissolved in rubber on the mill, the dissolved sulfur present in excess of saturation at room temperature separates on standing within the rubber in dendritic form, which slowly changes to rhombic crystals, which grow in size. Usually more or less rhombic sulfur will crystallize on the surface to form a bloom, especially if the surface has been disturbed. When the compound is vulcanized, the larger crystals of sulfur melt, and slowly go in solution in the rubber. The area surrounding the liquid sulfur droplets becomes vulcanized excessively, and appears as a bright spot in the sheet if a composition has been selected which does not discolor sufficiently during vulcanization to obscure the effect. If the stocks are allowed to stand longer than 24 hours before vulcanization, as is frequently the case, the sulfur crystals grow in size and the heterogeneous or spotty condition is increased. Although this spotty condition appears to exist throughout the sheet, crystallization or blooming of sulfur on the surface of the uncured slab results in severe spotting of the surface of the sheet. This is believed to be due to the spreading of the molten sulfur droplets on the surface in contact with the mold.

The spots become more apparent as the time of cure is advanced and are most evident after an extensive overcure. Vulcanized specimens showing this condition were photographed by placing sheets 0.19 cm. thick on an opal glass plate, 12.7 cm. from a light source of 2000 watts intensity, using an exposure of 1 minute at F-90 with Plenachrome film.

The spotty condition is exaggerated in compounds which vulcanize rapidly at a relatively low temperature. To determine the effect of several variables on spottiness the following base compound was selected:

Crepe rubber	100.0
Zinc oxide	3.0
Stearic acid	1.25
Tetramethylthiuram monosulfide	0.40
Zinc dimethyldithiocarbamate	0.10
Sulfur	Variable

Experiments in which stearic acid was eliminated and the zinc oxide reduced to 0.5 part resulted in no change in the spotty condition of the vulcanized sheets; this shows that sulfur plays the major rôle in causing heterogeneous vulcanization in this particular compound.

EFFECT OF SULFUR CONTENT

Compounds were prepared by adding 1, 1.5, 2, 2.5, 3, and 4 parts sulfur to the base compound, and allowing the stocks to stand several days at room temperature before vulcanization. Vulcanization was carried out for various periods at 109° and 127° C. The stocks were milled 12 minutes at 55° to 60° C after sulfur addition.

Spottiness was absent in all compounds containing 1.0 part of sulfur at all cures. It showed up faintly in the compound containing 1.5 parts and distinctly

in the compounds with 2.0 and 2.5 parts of sulfur. Spottiness was most pronounced in the compounds containing 3.0 parts of sulfur. The compound containing 4.0 parts of sulfur was practically free from spottiness at optimum cure, but showed considerable spottiness when cured for twice the optimum length of time. The optimum was judged in all cases by the development of the first maximum product of modulus at 600 per cent elongation and tensile strength. The spotty condition was consistently less pronounced in sheets cured at 110° C, compared with those cured at 127° C.

The reduced spottiness in the compound containing 4.0 parts of sulfur is due to the fact that some of the sulfur was not dissolved and formed a nucleus for internal crystallization which lessened surface bloom. This effect has already been noted by Twiss[20].

TABLE VII

EFFECT OF AMOUNT OF SULFUR AND TEMPERATURE OF VULCANIZATION ON PHYSICAL PROPERTIES AND TEMPERATURE COEFFICIENT

Sulfur added, parts [a]	Vulcanization temp. (° C)	Optimum [b] Vulcanization time (Min.)	Tensile strength (Kg. per sq. cm.)	% elongation	Load at 600% elongation (Kg. per sq. cm.)	10° C temp. coefficient [c]
1.0	109.4	60	283	810	67	1.8
	126.1	22.5	204	800	42	
1.5	109.4	45	276	750	102	2.0
	126.1	15	248	765	74	
2.0	109.4	45	304	735	132	2.2
	126.1	12.5	260	785	74	
2.5	66.5	2880	292	740	134	2.4
	109.4	35	315	680	204	2.2
	126.1	10	271	765	88	
3.0	66.5	2700	301	720	151	2.4
	109.4	25	271	730	127	2.0
	126.1	10	264	755	98	
4.0	66.5	2520	272	675	186	2.6
	109.4	20	288	760	106	2.0
	126.1	7.5	257	675	160	

[a] Base compound: crepe rubber 100.0, zinc oxide 3.0, stearic acid 1.25, tetramethylthiuram monosulfide 0.40, zinc dimethyldithiocarbamate 0.10.
[b] Appearance of first maximum product of tensile strength and modulus at 600 per cent elongation.
[c] Determined by equivalent moduli for undercures.

The effect of variations in sulfur content on the vulcanization of soft rubber is indicated in Table VII. The lowest temperature coefficient was found in the compound containing 1.0 part of sulfur, and the highest values resulted from higher contents of sulfur and lower temperatures of vulcanization. It appears, then, that the temperature coefficient of the rate of vulcanization may be influenced by heterogeneous dispersion of the sulfur. In the case of the compound containing 1 part of sulfur, it is certain that this sulfur was completely and uniformly in solution during vulcanization, since the solubility of sulfur at room temperature is over 1 per cent. It is recommended that future work in determining temperature coefficients of vulcanization rate be carried out on compositions where it is certain that the sulfur, accelerators, and activators are all in uniform solution during vulcanization.

It is of interest to compare the temperature coefficient for increased rate of vulcanization for 10° C temperature increase with the temperature coefficient for vapor pressure of sulfur. The temperature coefficient for vapor pressure of sul-

fur was obtained from Gruener's data in Figure 8 (*left*). The average values range from 2.6 to 2.2 in the temperature range 70° to 120° C. The agreement between the published 10° C temperature coefficients for increased vulcanization rate[8], and the above values for temperature coefficient of vapor pressure of sulfur is excellent. The increase in the rate of vulcanization of rubber with increased temperature depends in part on the increase in the vapor pressure and diffusion of sulfur resulting from an elevation of temperature. This would be expected, since reactivity depends on collision of sulfur atoms with the unsaturated carbon atoms in the rubber hydrocarbon.

EFFECT OF VARIATIONS IN MIXING AND STORAGE CONDITIONS

The effects of milling time after sulfur addition and of time of storage between mixing and vulcanization were investigated; batches were used of the test formula containing 3.0 parts of sulfur, milled 1, 3.25 and 14 minutes, respectively, at 70-80° C after the sulfur addition. Test sheets were vulcanized at 127° C after various periods of compound storage at room temperature and 90 per cent relative humidity. The results of these tests are given in Table VIII, and represent the complete range of test values for several test specimens. No results for breaks outside of restricted section are included. The results show that, when the sulfur is not dissolved in the rubber at the time of vulcanization, the rate of vulcanization is decreased and the quality of the vulcanizate is lowered. When the stock is allowed to stand 24 hours before vulcanization, the sulfur diffuses and partly dissolves in the rubber, and the vulcanization rate increases to normal. The strongest and most uniform vulcanizates were obtained by dissolving the sulfur in the rubber on the mill and allowing the stock to stand the shortest time before vulcanization.

These erratic results serve to show some of the large variations which may occur in certain rubber compounds unless mixing and storage conditions are carefully considered and properly controlled. These results also show that the time of storage at room temperature has a profound effect on the physical properties of the rubber, especially in the case of overcured samples. The effect of storage was greatest in the case of the stocks which were milled the longer period after sulfur addition, and vulcanized 24 minutes. Breaks in jaws and very low tensile values were found to be associated with the presence of large overcured spots. The development of spottiness or heterogeneity is shown in Figures 10 to 16.

The difficulties encountered by various laboratories in duplicating test results on separate batches of the same compound are well recognized. The present work showing the effect of varying the milling schedule and time of storage will account for some of the variations encountered.

Since wide differences must necessarily exist in the preparation and properties of different stocks, obviously it has not been possible or practical to specify standard conditions for milling, storing and handling which could be applied generally.

Present variations in laboratory and factory practices in the mixing and handling of rubber compounds are both numerous and extensive, and will undoubtedly remain so in view of the nature of the work and objectives to be achieved. Rubber research, however, has suffered from this situation, owing to lack of knowledge in the control of the variables which are involved in processing rubber, to say nothing of the variations in the raw materials. This frequently

leads to wrong conclusions being drawn by ascribing differences in physical data to the wrong variable in the experiment.

Some progress in the standardization of rubber processing for laboratory testing has been made by the Physical Testing Committee[1]. Much more effort

TABLE VIII

EFFECT OF SULFUR DISPERSION ON VULCANIZATION

Conditioning period after mixing (Days)	Vulcanization [a] period at 127° C (Min.)	Tensile strength (Kg. per sq. cm.) Before aging	Tensile strength (Kg. per sq. cm.) After aging [b]	Elongation at break (Per cent)	Load at 500% elongation [c] (Kg. per sq. cm.)
1-MIN. MILLING TIME AFTER SULFUR ADDITION					
0	12	172-186	197-250	830-870	0-14
1		242-295	49-141	590-640	105-137
4		91-235	102-116	420-590	X-148
7		32-270	18-162	270-610	X-155
11		211-274	141-183	560-615	119-127
0	24	264-292	144-183	630-650	88-105
1		225-281	102-193	600-650	67-112
4		246-267	25-120	630-640	84-91
7		232-267	0-190	620-640	77-91
11		197-274	74-155	600-650	81-119
3.25-MIN. MILLING TIME AFTER SULFUR ADDITION					
0	12	155-193	211-267	890-940	0-7
1		235-302	158-193	600-630	112-119
5		207-316	144-179	545-610	151-158
8		267-288	98-197	565-580	169-172
11		250-292	109-155	570-600	148-154
0	24	257-299	134-155	610-640	112-119
1		218-271	148-179	590-620	98-105
5		232-260	39-172	590-610	119-119
8		235-253	28-176	580-600	109-112
11		176-246	39-67	560-600	98-112
14-MIN. MILLING TIME AFTER SULFUR ADDITION					
0	12	292-299	193-225	670-670	74-84
1		236-278	14-148	570-600	134-141
5		197-253	4-46	570-600	123-127
7		239-257	32-46	600-610	116-120
11		35-211	0	370-580	X-116
0	24	229-267	176-176	590-610	109-116
1		239-257	21-102	600-610	102-116
5		21-179	4-7	320-560	X-105
7		134-190	11-18	520-570	106-116
11		7-46	0	220-390	X

[a] The best cure established by following A. C. S. methods [1] was found to be 12 minutes at 127° C.
[b] 7 days in air oven at 70° C.
[c] X denotes no test possible.

however is required in this field to reduce the variations still existent in the preparation and testing of rubber compounds.

DISCUSSION

It is apparent that heterogeneous vulcanization might also result from a non-uniform dispersion of accelerators or activators. For example, Morris[11] found

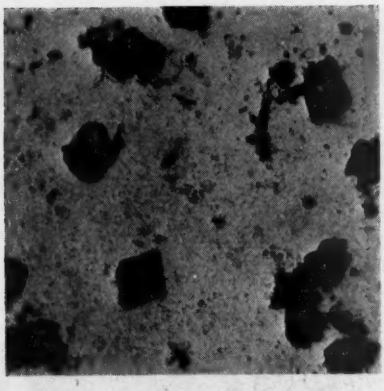
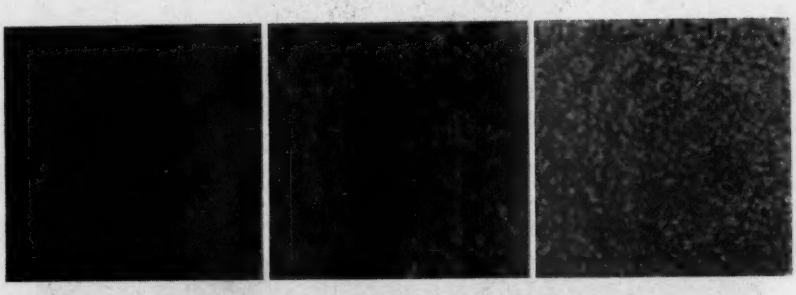


FIG. 10.—Unusual form of sulfur crystals in masticated crepe resulting from absorption of sulfur at 56° C.

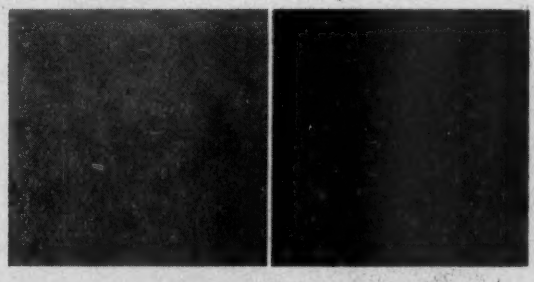


A. 3 parts sulfur in base compound, no storage before cure.

B. 3 parts sulfur in base compound, 1-day storage before cure.

C. 3 parts sulfur in base compound, 11-day storage before cure.

FIG. 11.—Absence (*A*) and presence (*B*, *C*) of spots in vulcanized rubber sheet cured 24 minutes at 20 pounds (× 1).



A. 1.5 parts sulfur in base compound.

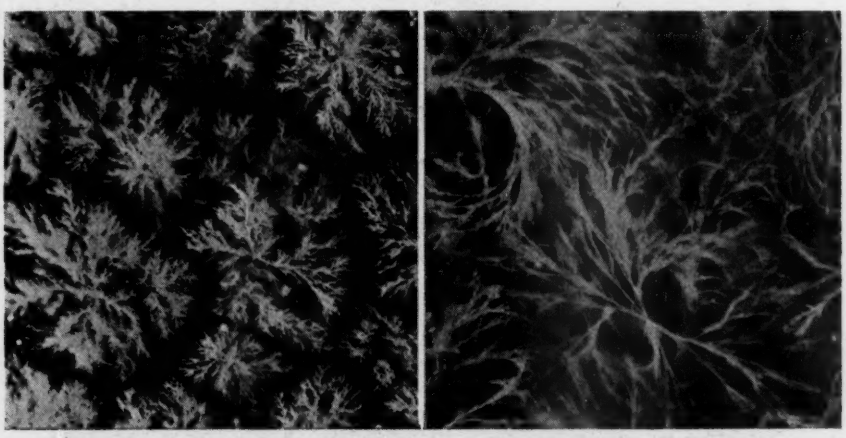
B. 3 parts sulfur in base compounds.

FIG. 12.—Absence (*A*) and presence (*B*) of spots in vulcanized rubber sheet stored 3 days before cure for 30 minutes at 20 pounds.

FIG. 13.—Effect of dusting sulfur on rubber surface, containing 1 part sulfur in the base compound, before cure at 25 minutes and 20 pounds (× 1).

FIG. 14.—Sulfur spot on surface of vulcanized rubber with sulfur bloom around spot (× 55).

that mercaptobenzothiazole and tetramethylthiuram disulfide are soluble in rubber to the extent of about 1 per cent at 100° and about 2 per cent at 127° C. Both of these accelerators are practically insoluble in rubber at ordinary temperature. It is readily realized therefore that a large proportion of these accelerators is likely to be partly in solid dispersion rather than in solution in the rubber at the start of vulcanization. Uniform distribution of accelerators will probably not take place during vulcanization because of their low diffusion rate in rubber. This condition would result in local spots in the rubber which have high accelerator concentration. It appears, therefore, that heterogeneous vulcanization is the result to be expected, judged from present practice in mixing and vulcanizing.



A. 2 per cent sulfur in masticated crepe (× 22). *B.* 3 per cent sulfur in masticated crepe (× 30).

FIG. 15.—Presence of dendritic sulfur in rubber after standing 2 days.

In a recent investigation carried out by Williams[24], it was shown that vulcanized rubber can be separated into fractions which contain different quantities of combined sulfur. The cause of this heterogeneity can now be explained, in view of the present investigation, as due to uneven distribution of reactants during vulcanization.

Numerous investigators have shown that the rate of chemical combination of sulfur with rubber during vulcanization does not increase in proportion to the amount of sulfur present, but the explanation has not previously been made clear. The effect of heterogeneous dispersion of sulfur and accelerators during vulcanization has not been given sufficient consideration in past studies of the vulcanization reaction.

In high-sulfur stocks, most of the sulfur exists as a solid dispersion in the rubber. As the temperature is increased, this dispersed sulfur gradually enters into solution by diffusion. The rate of solution will depend on the temperature, fineness of dispersed sulfur, rate of reaction of sulfur with the rubber, total amount of sulfur present, and changing solubility and rate of diffusion of sulfur in the rubber during all stages of vulcanization. The action of accelerators also will depend on diffusion and solubility phenomena.

FIG. 16.—Effect of 3 per cent sulfur in masticated crepe after standing for 14 days at room temperature (× 90).

Above. Presence of sulfur dendrites.
Below. Result of transformation of dendritic to rhombic sulfur.

REFERENCES

[1] Am. Chem. Soc., Div. of Rubber Chem., Physical Testing Comm., *Ind. Eng. Chem.*, **17**, 535 (1925); **20**, 1245 (1928).
[2] Brown and Muir, *Phys. Rev.* [2] **41**, 111 (1932).
[3] Endres, *India Rubber World* **68**, 635 (1923).
[4] Endres, U. S. Patent 1,875,372 (1933).
[5] Graffe, *Rubber Age* (London) **13**, 104 (1932).
[6] Gruener, *J. Am. Chem. Soc.* **29**, 1396 (1907).
[7] Kelly and Ayers, *Ind. Eng. Chem.* **16**, 148 (1924).
[8] Kemp and Ingmanson, *Ind. Eng. Chem.* **29**, 782 (1937); *Rubber Chem. Tech.* **10**, 743 (1937).
[9] Loewen, *Gummi-Ztg.* **27**, 1301 (1913).
[10] Loewen, *Kautschuk* **4**, 243 (1928).
[11] Morris, *Ind. Eng. Chem.* **24**, 584 (1932).
[12] Neumann, *Z. physik Chem.* **A171**, 416 (1934).
[13] Rimpel, *J. Soc. Chem. Ind.* **37**, 595A (1918).
[14] Ruff and Graf, *Ber.* **40**, 4199 (1907); *Z. anorg. Chem.* **58**, 209 (1908).
[15] Sager and Sucher, *J. Research Natl. Bur. Standards* **22**, 71 (1939).
[16] Schumacher and Ferguson, *Ind. Eng. Chem.* **21**, 158 (1929).
[17] Skellon, *India-Rubber J.* **46**, 251, 723 (1913); *Kolloid-Z.* **14**, 96 (1914).
[18] Taylor, Herrmann, and Kemp, *Ind. Eng. Chem.* **28**, 1255 (1936).
[19] Taylor and Kemp, *Ind. Eng. Chem.* **30**, 409 (1938).
[20] Twiss, *Trans. Inst. Rubber Ind.* **3**, 386 (1928); *Rubber Chem. Tech.* **1**, 346 (1928).
[21] Venable and Green, *Ind. Eng. Chem.* **14**, 319 (1922).
[22] West and Menzies, *J. Phys. Chem.* **33**, 1887 (1929).
[23] Williams, in Davis and Blake's "Chemistry and Technology of Rubber", A. C. S. Monograph No. 74, New York, Reinhold Pub. Corp., **1937.**
[24] Williams, *Proc. Rubber Tech. Conf. London*, **1938**, 304; Rubber Chem. Tech. **12**, 191 (1939).
[25] Williams and Kemp, *J. Franklin Inst.* **203**, 35 (1927); Lowry and Kohman, *J. Phys. Chem.* **31**, 23 (1927); Kemp and Malm, *Ind. Eng. Chem.* **27**, 141 (1935); **29**, 643 (1937).

HEAT CONDUCTIVITY OF RUBBER AT LOW TEMPERATURES *

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While examining the possibilities of applying rubber in low temperature work, we were hampered by the lack of available data on its physical properties at low temperatures. We were aware of the difficulties to be expected in making accurate measurements in that temperature region, and this applied especially to the heat conductivity, in which we were particularly interested. To obtain at least an estimate of the order of magnitude, we carried out some measurements of the heat conductivity of commercial rubber (North British tire rubber) at room temperature and at the temperature of liquid air.

We used the standard method, *i. e.*, heat transmission through a thin sheet, at both temperatures, with a small vacuum apparatus which had a circular cross-section of about 7 sq. cm. The specimen had a thickness of 0.9 mm. We checked the low-temperature measurement by the following method. A bag of the same rubber was immersed in liquid oxygen and filled with liquid nitrogen. The rate of evaporation of the nitrogen was then measured and this, together with the dimensions of the bag, allowed an independent determination of the heat conductivity. The mean values obtained by the two methods are as follows:

Temperature (absolute)	Heat conductivity (cal. per sec. per cm. per degree)
293°	0.00055
83°	0.000018 0.000010

This considerable drop in heat conductivity to, say, one-fortieth from room to liquid air temperature, does not seem to be confined to this particular rubber, for other specimens which we subjected to rough measurements showed a similar behavior.

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THE EFFECT OF SILENT ELECTRIC DISCHARGES ON RUBBER SOLUTIONS *

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INTRODUCTION

THE SIGNIFICANCE OF SILENT DISCHARGES IN THE CHEMISTRY OF HIGH-MOLECULAR SUBSTANCES

To the investigations of Berthelot and de Hemptinne[2] on the effects of silent electric discharges on organic compounds should be credited the discovery that polymerization can in many cases be induced by such treatment. Also of special significance is the discovery, toward the end of the last century, by the Belgian chemist, de Hemptinne, that mobile fat oils can be transformed by silent electric discharges, in an atmosphere of hydrogen, into highly viscous oils. Based on this phenomenon, a technical process for the manufacture of valuable lubricating oil, the socalled Voltol, was successfully developed, and since that time this oil has become of considerable economic importance. A more thorough physico-chemical investigation of the phenomena involved in the formation of Voltol was carried out by Hock[3], following a suggestion of Nernst. In this work, the assumption was made that the electric discharges act on the individual fat acid residues through ionic and electronic collisions, which in turn cause polymerization of the corresponding molecules. In this way high-molecular compounds are formed, and these remain dissolved in a less polymerized mother liquid and thus impart a very high internal friction to the whole system.

Hock was further able to show[3] that, in addition to these compounds, polymers are formed which are insoluble in the oil and separate in the form of small flocculates, the socalled "Voltol fish". To a certain extent these resemble white factice, a material formed from oil and sulfur, and they are insoluble in all organic solvents. According to present day views of the chemistry of high molecular substances, these polymers should have a three-dimensional network of original free chain-form molecules, so that attack by solvents does not continue beyond the stage of swelling.

In addition to these investigations, Eichwald and Vogel[4] studied the formation of Voltol, chiefly from the purely chemical and technical points of view, and proved that hydrogen is liberated by the action of electric discharges. This fact follows from the at first surprising result that, in an atmosphere of pure nitrogen, oleic acid, an unsaturated acid, is partially transformed into stearic acid, a saturated acid, under which conditions the liberated hydrogen atoms combine with oleic acid, while the oleic acid molecules, activated from a valence point of view by their loss of hydrogen atoms, combine at the same time to form high-molecular Voltol acids. That a chemically active gas is in general not necessary for the formation of Voltol was shown by Hock in the work already mentioned[3], in which it was found that Voltol is formed in an atmosphere of argon.

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We owe to Becker[5] the production of pure hydrogen electrically from hydrocarbons, and the development of a particularly suitable laboratory apparatus for the experiments. According to the technique of Becker, a fine foam is formed from the liquid in the electric field through which the gas is conducted, so that the discharge is particularly effective. This apparatus was utilized subsequently by Hock and Nottebohm[6] in further work on the polymerization of fat oils, and also by Hock and Fromandi[7] in their first experiments on the exposure of rubber solutions to the action of silent electric discharges.

Whereas in the past the idea had been to polymerize substances of low molecular weight by the electric method, with the ultimate view in some cases of obtaining highly polymeric compounds, *e. g.*, the polymerization of decalin (decahydronaphthalene) to a shellac-like flaky product[7], in the work described in the present paper experiments were concerned for the first time with the effect of electric discharges on substances which were already in a high-molecular state. In this case it seemed probable that there would be either a breakdown of large molecules to smaller molecules or a building up of already large molecules to still greater molecular units, in the latter case either by a lengthening of the molecular chains or by the formation of a network structure.

Since a network with sulfur atoms as structural units[8] represents theoretically the state of ordinary vulcanized rubber, the structure mentioned above might be regarded as an electric vulcanizate of rubber with rubber. In the experiments of Hock and Fromandi[7], solutions of natural rubber and also solutions of synthetic isoprene rubber (sodium-isoprene rubber from polymerized isoprene) were exposed to electric discharges, with the result that in most cases breakdown of the molecules took place, a phenomenon characterized by a considerable decrease in internal friction of the solutions and by other changes.

In the case of isoprene rubber, however, the molecular size unexpectedly increased at the beginning, and this change was accompanied by other characteristic changes; but this increase very soon stopped and the molecular size then decreased. This discovery induced the authors to carry out the confirmatory experiments described in the present paper, particularly since unpublished experiments by Hock and Wagner in 1933 on natural rubber had shown that the size of the molecules can be increased to the point where an insoluble form of rubber is obtained.

The polymerization of isoprene to rubber, of butadiene to Buna, etc., under the influence of catalysts represents reactions which proceed spontaneously, whereby activated molecules capable of forming chains are formed by a primary reaction with expenditure of a definite heat of activation. These chain molecules then arrange themselves side by side in such a way that the individual chains form a network. The process finally comes to a stop by rupture of any chain.

Polymerization by the action of silent electric discharges differs fundamentally from this mechanism in that activation of the molecules or molecular constituents is effected by an external force of some kind. In the case of spontaneous polymerization, the activation process is perhaps the slowest process of all, and therefore it is the one which governs the order of the reaction (as in the thermal polymerization of styrene to polystyrene, which both Mark and Raff[9], and Schulz and Husemann[10] in 1936 studied from the kinetic point of view). In contrast to this, chain growth proceeds at a relatively high rate. On the other hand, in the case of polymerization under the influence of silent electric discharges, the activation by an external force governs the course of the reaction.

The rate of polymerization therefore depends primarily on the electric conditions, and the progress of the reaction remains to a considerable degree independent of the temperature.

It becomes possible in this way to set in motion, through activation by an external force, a reaction which otherwise would not progress at all spontaneously. In its present state, the application of the method of silent electric discharges to the chemistry of highly polymeric substances means that new possibilities are placed at one's disposal for synthesizing substances of progressively higher molecular weights.

PROBLEMS INVOLVED IN THE PRESENT INVESTIGATION

In contrast to the careful experiments of Hock and Fromandi[7], which showed that natural rubber in solution is broken down chemically by electric treatment, it was later found possible to build up ordinary rubber molecules into larger molecules, as had already been indicated by the experiments of Hock and Fromandi on isoprene rubber. In view of this, a continuation of the work in the same direction seemed, even at that time, to be of promise. In the experiments of Hock and Wagner, already mentioned, the results of Hock and Fromandi were provisionally accepted as established in that it was considered that if the experiments were repeated, no polymerization of natural rubber would take place. If it were assumed, however, that the addition of even the smallest quantities of chemically active substances, *e. g.*, iodine trichloride, to hydrogen might lead to the formation of unstable compounds of rubber with iodine or chlorine, it would then be possible, by subsequent decomposition of these molecules, to obtain more reactive molecules, and thus to bring about polymerization. Experiments seemed to confirm this supposition, but when the experiments were repeated without the addition of such reagents precisely the same results were obtained.

The fact is that when the hydrogen was very carefully purified and even traces of oxygen were removed, a synthesis of the rubber molecules to larger molecules instead of a breaking down took place. Hock and Fromandi[7] themselves made careful attempts to purify the hydrogen which they used, but this was not done so thoroughly as was done later for the first time in an intelligible way, after Staudinger and Dreher[11] had shown so convincingly, in their exact experiments on the viscosity of rubber solutions, the effect which even mere traces of oxygen have on the molecular size of rubber. Even a few atoms are sufficient to rupture chains here and there, with formation of molecular fragments. The first experiments on polymerization in which attention was paid to this fact were carried out in collaboration with A. Rosenberg, to whom thanks are due for his contribution to the work.

From these experiments a general procedure for the work described in the present paper was planned, direct advantage being taken of the experiments of Hock and Fromandi to use only hydrogen gas which had been completely freed of oxygen.

The experiments were carried out on the one hand with natural rubber (benzene solutions of crepe) and on the other hand with synthetic rubber (Zahlenbuna and Buna 85)[12]. As in the polymerization of fat oils, the process can be continued not only to the point where an increasingly viscous solution is formed, but also to the point where a flaky gel-like substance separates, which after purification is found to be an insoluble form of rubber with a

three-dimensional network structure, in accord with its synthesis. Both natural rubber and Buna rubber can be polymerized to these states. Of course the final products of this method of polymerization lack all of the elasticity and plasticity which are so characteristic of rubber. However, when the polymerization is restricted so that the highest polymers formed remain soluble, then plastic and elastic forms of rubber are obtained, which in some respects, including tackiness and solubility, still closely resemble natural rubber.

The problem resolved itself therefore into the development of methods for obtaining these various stages of polymerization, for separating the individual fractions, for purifying these fractions and for characterizing their properties. Also there was the problem of determining whether it was possible, by the addition of other polymerizable substances during the electric treatment, to obtain products consisting of mixed polymers with rubber or Buna. Finally it seemed desirable to study the technical importance of the new types of rubber, insofar as this was possible with the limited quantities which were prepared in the laboratory experiments[13].

Insofar as the technical aspects of the work are concerned, the investigation described in the present paper, which was carried out with the aid of the Minister of Commerce, is part of a more comprehensive problem in the automotive industry. In addition to the possibilities offered by the present technique of manufacturing tires and by current factory methods, ways and means are to be sought to increase the heat resistance of automobile tires, or to improve their heat economy. Since tires and the vulcanized rubber mixtures which compose them are not ideal elastic bodies, a more or less large percentage of the work absorbed in the elastic effects during operation is transformed into heat, and the greater the load and the higher the speed, the greater is this transformation of work into heat. Furthermore, since rubber is a poor conductor of heat, there is only an incomplete loss of heat, and therefore a corresponding increase in the temperature during operation. Under particularly unfavorable conditions, this internal heat may lead to chemical decomposition, *i. e.*, to destruction of the rubber, which renders the tire useless. But even before this happens, the tensile strength and elastic properties of the rubber are so badly affected that the tire may become prematurely unfit for service at high speeds or under heavy loads.

To increase the serviceability of tires above present standards, an improvement in their heat economy is necessary. It is possible to attain this in various ways. For example, an attempt can be made to increase the heat conductivity of rubber by adding materials of higher conductivity than that of the rubber, provided that they do not impair the technically important properties of the mixtures. Then again efforts can be made, as was done in the present work, to produce new types of rubber, which might be found to have inherently greater resistance to heat. Although these polymers are more highly polymerized than the material from which they are made, and therefore have less tendency to soften and decompose, they still allow the hope that, in the vulcanized state, they may be more resistant to heat, so that elevated temperatures are less destructive to them than to ordinary rubber. Here it must of course be assumed that the greater resistance to heat which may be obtained is not offset by a higher energy loss of the new type of rubber; in other words, the "damping" of mixtures prepared from these polymerized rubbers should be no greater than before; otherwise the tires would develop higher temperatures. Even if the tires withstand these higher temperatures, there is still nothing in general

to be gained. There is absolutely no reason, however, to expect an increase in the degree of polymerization to be accompanied by an increase in energy loss, *i. e.*, a damping effect. It has not been the aim of the preliminary part of the investigation described in the present paper to settle these technical problems; rather it has been limited in the beginning to an investigation of the possibilities of transforming natural rubber and artificial rubber by means of silent electric discharges. The idea in this case was to increase the degree of polymerization, although within such limits that the valuable elastic and plastic properties of the original rubber would not be impaired. The experiments concerned with technical mixings were intended merely to prove that the new types of rubber not only represent chemical products with special properties, but also that they have the essential properties considered necessary for ordinary technical processing. Whether these properties meet expectations in the ways just pointed out can be proved only by a further series of experiments still to be carried out.

THE REACTION APPARATUS

The electric discharges were produced in an apparatus which was similar to that used by Hock and Fromandi[7], but in which several important changes were made (see Figure 1).

In principle the apparatus was, as before, a Siemens ozone tube. Two concentric glass tubes *a* and *b*, sealed tightly by the ground glass section *A*, enclose a space between them which serves as the reaction chamber, 5 mm. wide. Tube 6 is surrounded by a cooling jacket *c*, within which electrode E_1, in the form of a copper wire, is suspended. From the regulating stopcock *H*, purified hydrogen passes through a fine-pored sieve plate or glass frit *S* in the discharge chamber *R*, where it breaks up the reaction mixture into fine particles and creates a foam, which is greatly increased by application of the high tension discharge.

The circulating liquid passes through *d* into two foam traps e_1 and e_2, is broken up in these traps, and then flows through *f* back again into reaction chamber *R*. The valve *g* serves as an outlet for the treated solution; *h* leads to the water jet pump, and *M* is a manometer which shows the pressure within the apparatus.

The apparatus acts as a condenser. The inner tube *a* serves as a second electrode E_2, which contains a saturated sodium chloride solution as the electrode liquid.

The alternating current was obtained by the same method used by Hock and Fromandi[7] and by Hock and Nottebohm[6], and described by these workers. The voltage was approximately 5000, the frequency approximately 500 per second.

PURIFICATION OF HYDROGEN

The importance of the hydrogen being free of oxygen has already been mentioned. A particularly careful method for preparing pure hydrogen was developed, with the use of an apparatus, the principle of which was suggested by that of Kautsky and Thiele[14].

Hydrogen, obtained from an ordinary supply cylinder, passed through a fine-pore porcelain cell into a column approximately 1 m. high, of 20 per cent sodium hydrosulfite. Indigo was added to this solution as an indicator; on reduction to indigo white the solution turned yellow. As soon as the solution was consumed, the color changed to blue as a result of oxidation of the indigo white to indigo by oxygen. Since absorption of oxygen takes place at low temperatures, the absorption tube was provided with a cooling jacket with circulating water.

From here the hydrogen passed through a condenser which could be cooled with carbon dioxide snow to freeze out any water vapor contained in the hydrogen, and thence through a tube, approximately 30 cm. long, which was filled with active A-carbon (regenerated periodically in a vacuum heater), next through a layer of phosphorous pentoxide 40 cm. long, and finally through the regulating stopcock *H* into the electric discharge apparatus.

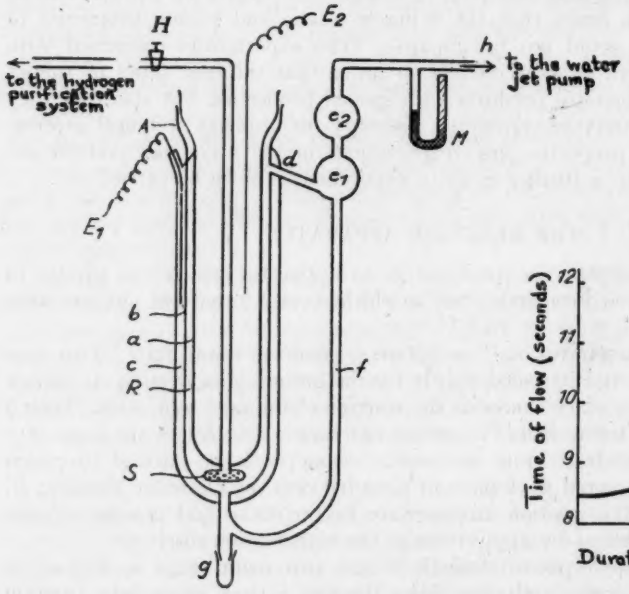

FIG. 1.—The reaction apparatus.

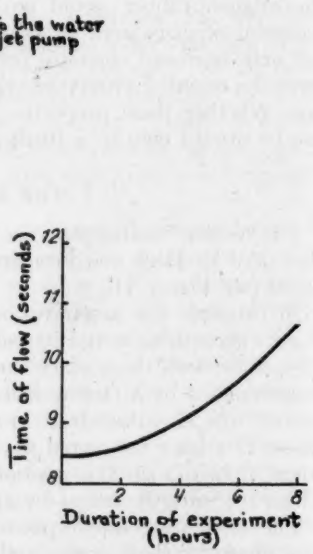

FIG. 2.—Increase in the internal friction of decalin alone.

EFFECT OF ELECTRIC DISCHARGES ON PURE SOLVENTS

DECALIN

Since it was possible to expose rubber to electric discharges only when it was in solution, it was necessary to determine first of all whether the pure solvents themselves were changed in any essential way by exposure, in an atmosphere of hydrogen, to the action of electric discharges. Decalin (decahydronaphthalene) was chosen as the first solvent to be investigated. With this substance, as in all subsequent experiments, the procedure was to fill the discharge chamber *R* two-thirds full, *i. e.*, approximately 250 cc. with decalin, evacuate with a water jet pump, and flush out with hydrogen until all air was driven out. The current of hydrogen was then so regulated that the manometer *M* indicated a pressure of 19-20 mm. of mercury in the discharge chamber.

To prevent absolutely any inflow of air, care was taken throughout that outside, *i. e.*, beyond the regulating stopcock *H*, there was an excess pressure of 40-50 mm. (mercury) of hydrogen at all times. To be able to observe this pressure at any moment, a second manometer was installed between the purification system and the reaction apparatus.

When all the precautions described had been taken, the alternating current was turned on and so regulated that the current strength was 0.2 ampere in the

exciter circuit and 0.45 ampere in the primary circuit, with a voltage of 110. This corresponded to approximately 10 milliamperes and 5000-5500 volts in the secondary circuit.

During an experimental run, the Voltol tube was strongly cooled by tap water. The temperature of the outflowing cooling water was 8-10° C; the temperature of the electrode solution in tube *a* was approximately 15° C.

Immediately after application of the electric current, the decalin began to foam considerably; this foam spread through tube *d* into the large bulb e_1, liquified at this point, and the liquid flowed through *f* back into the reaction chamber *R*. This continuous cycle meant that a new surface of liquid was continuously exposed to the electric discharge, so that all of the decalin in the apparatus was uniformly "electrified". After exposure to the electric discharge for about one hour, the decalin assumed a yellowish color, perhaps as a result of slight oxidation (residual moisture of the once-vacuum distilled decalin). As in the experiments of Hock and Fromandi[7], the exposure was continued for 8 hours, with an applied voltage of 6200 instead of 5000, in order to correlate the results with other measurements made with the same apparatus. At the end of each hour, the experiment was interrupted to remove a small sample and determine its viscosity.

Figure 2 shows the experimental results. In later experiments with rubber solutions, the duration of the experiments was 4 hours at the most, and only 1 hour as a rule. In this length of time the decalin showed no increase in internal friction nor any tendency to form a precipitate, even when acetone was added. Accordingly the formation of a polymer of decalin as a disturbing factor was not to be feared, especially since voltages of only 5000 to 5500 were used in the electric treatment of the rubber solutions.

Benzene

Benzene was exposed to an alternating electric discharge, with an exciter circuit of 0.2 ampere; a primary circuit of 0.45 ampere and 110 volts; a secondary circuit of 5500 volts (approximately 500 cycles per second); an excess pressure of the entering hydrogen of 45 mm. of mercury; and a pressure within the reaction chamber of 38 mm. (as a result of the higher vapor pressure of benzene).

During the experiments, the apparatus was cooled by ice-water, which flowed out at a temperature of 6-8° C.

No increase in viscosity could be detected after 4 hours' exposure; in fact aside from a yellow coloration, no significant change in the benzene was noticeable. Accordingly, as with decalin, no complications were to be expected when benzene was used as solvent. The same result was obtained with toluene.

Pyridine

The procedure followed with pyridine was the same as with benzene, except that the pressure in the reaction chamber was again 20 mm. of mercury, and tap water at 10° C was used instead of ice-water for cooling. No appreciable disturbing changes in pyridine by the action of electric discharges were observed.

THE EFFECT OF ELECTRIC DISCHARGES ON RUBBER SOLUTIONS

Natural Rubber

In the experiments with natural rubber, a fairly viscous solution (9 grams of rubber in 100 grams of solution of crepe which had first been masticated and

reprecipitated once by acetone) was used, in most cases in benzene, because with its much lower boiling point, this solvent could be more easily evaporated than decalin from the solution. However, as a result of its rapidly increasing viscosity, the solution could no longer circulate after exposure to electric discharges for one hour. A tough, extremely adhesive gel formed on the inside of the apparatus, and this gel could be removed only by scraping.

By precipitation with acetone of the rubber which still remained soluble, an apparently less highly polymerized form of rubber was isolated. This product was dried at 50° C in a vacuum (1 mm. of mercury). It will be described later in this paper.

When a 6 per cent solution instead of a 9 per cent solution was exposed to electric discharges, circulation in the apparatus was more rapid, and only after 3 hours' exposure did it come to a standstill because of the formation of a gel.

A 3 per cent rubber solution, which was a relatively thin liquid, was then exposed for 6 hours to electric discharges. In this case there was no tendency to form a gel; nevertheless the dissolved rubber underwent marked changes, as is evident by an examination of the data in Table II.

Buna

With synthetic rubber the procedure followed was the same as with natural rubber. As representative of synthetic rubber, Buna-85 was used in most of the experiments. It was previously extracted with acetone, and here too 3, 6 and 9 per cent solutions were treated electrically. As far as superficial changes were concerned, solutions of Buna behaved, when exposed to electric discharges, exactly like solutions of natural rubber under the same conditions. No gel formed in the 3 per cent solution; a gel formed after one hour in the 6 per cent solution, and a gel formed after one-half hour in the 9 per cent solution, irrespective of whether the solvent was benzene or decalin.

These particular experiments showed that, when exposed to electric discharges, solutions of natural rubber and of Buna-85 undergo some sort of change which is manifest by an increase in internal friction and finally by the formation of a gel if the concentration is sufficiently high. When 1 per cent of the accelerator Vulkazit-P (based on the rubber content) was added to a 9 per cent solution of Buna-32, and the solution was exposed to electric discharges for 14 hours, the viscosity attained a value only 0.5 as great as that attained by a corresponding solution to which no accelerator had been added. Probably further investigations in this direction would lead to the discovery of substances which accelerate polymerization by electric discharges and even play a part in determining its character.

EXAMINATION OF THE POLYMERIC PRODUCTS

Natural Rubber

viscosity

The increase in viscosity, which occurs when rubber solutions are "electrified", and which may lead to actual gel formation, is evidently the result of polymerization, the progress of which can be followed by determinations of the internal friction.

An Ostwald viscometer was used for measuring the viscosity. With 3 per cent solutions the diameter of the capillary was 1 mm.; with 6 per cent solutions it was 1.5 mm. The length was 8 cm.; the capacity 2 cc. The measurements

were carried out at 20° C in a thermostat. Since efforts were made only to obtain relative values, the measurements were confined to the times of flow in seconds.

As Table I and Figures 3 and 4 show, the increase in viscosity was at first slow, then became progressively more rapid. The data refer to solutions containing 3 and 6 per cent of crepe rubber in benzene, which were exposed to electric discharges, with ice-water circulating through the cooling jacket of the reaction tube.

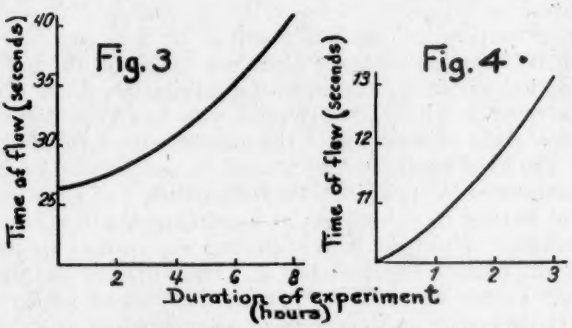

FIG. 3.—Times of flow of a 3 per cent benzene solution of crepe rubber (d = 1 mm.).
FIG. 4.—Internal friction of a 6 per cent benzene solution of crepe rubber (d = 1.5 mm.).

TABLE I

INCREASE IN INTERNAL FRICTION BY POLYMERIZATION OF NATURAL RUBBER IN SOLUTION

Time of exposure hours	Time of flow (in seconds) 3% solution (diam. 1 mm.)	6% solution (diam. 1.5 mm.)
0	26.5	10.0
1	27.5	10.8
2	28.4	11.9
3	29.5	13.2
4	31.0	—
5	33.1	—
6	35.4	—
7	37.8	—
8	40.8	—

Since in these experiments a certain amount of benzene always volatilized into the vacuum of the discharge tube, a mark was placed on the apparatus, and the volatilized benzene was replenished hourly up to this mark.

IODINE NUMBER

The iodine number, which is the number of grams of iodine taken up by 100 grams of substance (rubber), does not give any direct indication of the degree of polymerization. But in the experiments described in the present work, the higher the degree of polymerization the lower was the iodine number, and therefore this value served as a direct measure of the degree of polymerization.

The method used for determining the iodine number was that of Kemp[15]. In principle this is a modification and application to rubber of the Wijs method of determining the iodine number as used in oil and fat analysis. The iodine

number of the untreated rubber, after purification by repeated solution in benzene and precipitation with acetone, was 362.0, compared to a theoretical value of 372.8. On the contrary the iodine number of the polymerized rubber obtained by treatment with electric discharges varied from 250 to 70 (for detailed data, see Table II).

SOFTENING TEMPERATURE

Parallel with the increase in viscosity and "molecular weight", and decrease in iodine number of the polymerized rubber, there was an increase in the softening temperature.

This softening temperature was determined in the following way.

A weight of 0.1 gram of rubber sample was placed in the lower part of a two-part cylindrical aluminum block oven (approximately 8 cm. high and 6 cm. diameter), the cover of which was equipped with two glass peepholes through which the sample could be observed. A thermometer was inserted through a hole in the cover. The oven was heated by a small flame. As soon as the surface of the sample commenced to "perspire", the temperature was recorded. It was essential that the heating be carried out at a uniform slow rate, according to an established standard. When the time of heating was reduced to about one-half, the softening temperature increased 4-5° C. The softening temperature of the "non-electrified" rubber was 142° C; that of the treated rubber varied from 152° to 200° C, depending on the degree of polymerization.

HEAT OF COMBUSTION

Not only the iodine number but also the heat of combustion may serve as a criterion of the degree of polymerization. It has already been shown by Geiger[16] that the heat of combustion of the polycyclorubber which he prepared was 10548 calories per gram, and that of the untreated natural rubber 10700 calories per gram, *i. e.*, about 1 per cent lower[17].

In accord with this, the soluble and insoluble polymers obtained in the present work showed decreases in the heats of combustion of 2.5 to even 20 per cent.

The heats of combustion were measured in a Roth microbomb[18]. Natural rubber, in the form of crepe reprecipitated once by acetone, which was used as the starting material in the polymerization experiments, gave a heat tone of 10.71×10^3 calories. Further data are given in Tables II and III.

ELEMENTARY ANALYSIS

That the modified rubber samples obtained by the action of silent electric discharges were actually polymerized products was proved by elementary analyses carried out in the combustion apparatus of Reihlen-Weinbrenner. The products obtained by "electrification" of rubber had the same composition as the starting material, *i. e.*, the composition $(C_5H_8)_x$ of polyprene, *i. e.*, 88.15% carbon and 11.85% hydrogen.

SUMMARY OF THE INDIVIDUAL RESULTS OF ALL THE EXPERIMENTAL METHODS AND A COMPARISON OF THESE RESULTS

Natural Rubber

Table II summarizes the individual measurements of the iodine numbers, softening temperatures and heats of combustion. These data show that polymerization takes place even in a 3 per cent solution under the influence of alternating

discharges, that it becomes appreciable under the same conditions in one-half the time in a 6 per cent solution, and that a highly polymerized, insoluble rubber product with properties wholly different from those of the original rubber is formed in a 9 per cent solution after only 1 hour of exposure to the electric discharges.

TABLE II

PROPERTIES OF POLYMERS FROM NATURAL RUBBER

Concentration of benzene solution (percentage)	Time of exposure (hours)	Soluble or insoluble	Iodine number	Softening temperature (° C)	Heat of combustion (calories per gram)
Solid	0	Soluble	362.0	142	$10{,}710 \times 10^3$
3	6	Soluble	256.0	146	$10{,}510 \times 10^3$
6	3	Soluble	223.0	153	$10{,}390 \times 10^3$
9	1	Soluble	223.4	153	$10{,}395 \times 10^3$
9	1	Insoluble	70.0	200	$8{,}690 \times 10^3$

TABLE III

PROPERTIES OF POLYMERS FROM BUNA-85

Concentration of benzene solution (percentage)	Time of exposure (hours)	Soluble or insoluble	Iodine number	Softening temperature (° C)	Heat of combustion (calories per gram)
Solid	0	Soluble	316.2	150	$10{,}615 \times 10^3$
3	7	Soluble	226.0	164	$10{,}520 \times 10^3$
6	3	Soluble	220.0	164	$10{,}450 \times 10^3$
9	1	Soluble	230.0	164	$10{,}440 \times 10^3$
9	1	Insoluble	160.1	210	$8{,}200 \times 10^3$

ELEMENTARY SEMIMICROANALYSIS

Untreated natural rubber (crepe reprecipitated once by acetone)

1.2826 g.	H_2O 5.8597 g.	CO_2 7.0585 g.
1.2609 g.	5.8370 g.	6.9886 g.
0.0217 g.	0.0227 g. H_2O	0.0700 g. CO_2

Hence C = 88.05% H = 11.70%

Polymers (the data are representative of numerous experiments)

2.2813 g.	H_2O 5.8816 g.	CO_2 7.1253 g.
1.2606 g.	5.8597 g.	7.0586 g.
0.0207 g.	0.0219 g. H_2O	0.0677 g. CO_2

Hence C = 87.98% H = 11.80%

The insoluble polymer which separated on the glass tube of the reaction vessel contained electrically atomized glass.

The determinations were made on samples which, in cases where they had not been converted into insoluble precipitates, had first been precipitated by acetone and dried in a vacuum (1 mm. of mercury) at 50° C. In the 6 per cent solution a tough gel formed on the inside electrode after 3 hours; in the 9 per cent solution it formed after 1 hour. In most cases the experiments, the primary object of which was to obtain the residual soluble polymer, were stopped at this point. By continuing beyond this point, it was possible to obtain larger quantities of the subsequently formed insoluble component by extracting the gel with a large proportion of benzene to remove the lower polymers and to separate the gel as fine flocculates.

The insoluble part was separated from the solution by a high-speed centrifuge (the ultracentrifuge of Fa. Padberg, Düsseldorf, n=36,000 per minute), was then washed with petroleum ether for 10 hours and finally was dried in a vacuum. The soluble polymer was precipitated from the mother benzene solution by the method already described. This soluble polymer had almost the same properties as those of the polymer formed in the 6 per cent solution.

BUNA-85

Parallel Experiments with Those with Natural Rubber

In the experiments with synthetic rubber, which were similar in every way to those with natural rubber, Buna-85 was available as the starting material. It was first extracted with acetone in a Soxhlet apparatus to remove substances which had been added to protect it from deterioration.

It is not necessary to describe in detail the procedure, methods of separation and determinations, for they were carried out in exactly the same way as with natural rubber. It is sufficient to give the results in summarized form as shown in Table III.

Table IV

Increase in Internal Friction During the Polymerization of Buna-85 in Solution

Time of exposure (hours)	Time of flow (seconds; d = 1 mm.)
0	40.5
1	41.5
2	42.8
3	44.0
4	45.5
5	47.0
6	48.0
7	51.9

Table IV and Figure 5 show the increase in viscosity of a 3 per cent benzene solution of Buna-85 as a function of the time of exposure to electric discharges.

A small sample of the low polymer Buna-32 also was available for experimentation, and a 9 per cent solution of this was studied by the same method to determine the increase in internal friction brought about by electric treatment. The results are shown in Figure 6.

In judging the value of the iodine number, it should be noted that even the original rubber had a lower iodine number, *viz.*, 316.2, than the value of 468.0 to be expected theoretically if, in the original polymerization, the butadiene underwent no cyclization or conversion into a network structure.

By washing with petroleum ether a considerable quantity of the insoluble gel which was separated by centrifuging, a large enough quantity of the soluble component still occluded in the gel was extracted by the petroleum ether for further investigation. It was found that this portion which was retained so tenaciously by the gel had properties which placed it between the soluble and wholly insoluble polymers, *e. g.*, its iodine number was 193, and its heat of combustion was 10.19×10^3 calories per gram.

That also in the case of Buna-85, "electrification" leads to the formation of polymers was proved by elementary analysis, which showed that the product had the same composition as that of the original material, *viz.*, $(C_4H_6)_x$.

Theoretical percentages of carbon and hydrogen for $(C_4H_6)_x$:

$C = 88.1$ $H = 11.19$

Actual weights:		
1.2846 g.	H_2O 1.4484 g.	CO_2 8.8091 g.
1.2591 g.	1.4232 g.	8.7262 g.
0.0255 g.	0.0252 g. H_2O	0.0829 g. CO_2

Hence C=88.65% and H=11.01%

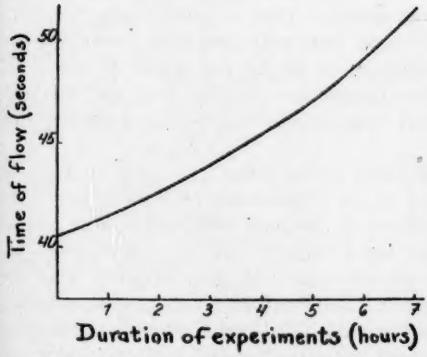

FIG. 5.—Times of flow of a 3 per cent benzene solution of Buna 85 (d = 1 mm.).

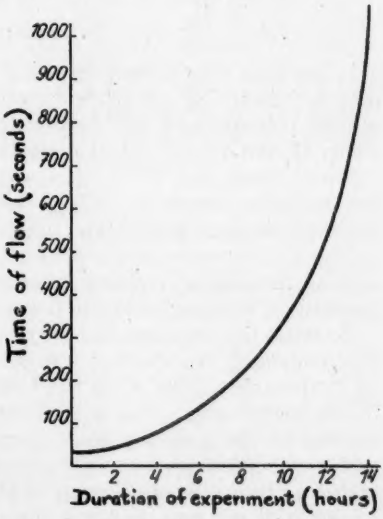

FIG. 6.—Times of flow of a 9 per cent benzene solution of Buna-32.

INFLUENCE OF THE SOLVENT AND OF THE TEMPERATURE ON THE COURSE OF THE POLYMERIZATION

With Buna-85 the influence of the solvent and the temperature on the course of the reaction and on the properties of the resulting polymers was studied. To assure comparable experimental conditions by preventing to the greatest possible extent volatilization of the solvent, the apparatus was kept cold with ice-water during the experiments. The separation of gels in decalin, benzene and toluene solutions was approximately the same after the same lengths of time.

The phenomena were of the same general character, whether the experiments were carried out at −25° C, 5° C or 50° C. Toluene was the solvent for −50° C, benzene for 5° C and decalin for 50° C, and in all cases 9 per cent solutions of Buna were employed.

Table V gives some representative experimental data which were obtained with a 9 per cent solution of Buna after electric treatment for 1 hour.

In all cases the changes which take place during these treatments depend fundamentally on activation of the molecules by electrical bombardment, and are independent of the temperature, which has an influence on the rate of the reaction only in the case of spontaneous activation.

TABLE V

ELECTRIC POLYMERIZATION OF BUNA-85 AT VARIOUS TEMPERATURES

Type of polymer	Solvent and Temperature	Softening temperature	Iodine number
Soluble	Polymerized in benzene at 5° C.	219.1	152°
	Polymerized in toluene at — 25° C.	220.0	152°
Insoluble	Polymerized in benzene at 5° C.	168.1	195°
	Polymerized in toluene at — 25° C.	180.0	193°

REPEATED ELECTRIC TREATMENT OF RUBBER IN SOLUTION

NATURAL RUBBER

It has been shown that, when a 9 per cent solution of natural rubber in benzene is "electrified", a gel is formed and that by centrifuging this product a soluble polymer and an insoluble polymer can be isolated. As is evident in Table II, the degree of polymerization of the soluble component is considerably different from that of the insoluble component. This is particularly evident by the iodine numbers and by the softening temperatures, and above all by the heats of combustion. The question then arose whether it would be possible, by renewed exposure to electric discharges, to increase the degree of polymerization of the soluble polymer after it had been separated from a considerable quantity of admixed insoluble polymer.

To settle this question, the gel was separated in the usual way by centrifuging. The remaining solution was concentrated to its original strength of 9 per cent by evaporation at 30° C of the large volume of benzene which had been added before centrifuging. It was then exposed for 1 hour to electric discharges. At the end of this time the newly formed gel was removed, was agitated with an excess of benzene and was then centrifuged. The residual solution was concentrated as before by distillation of the solvent at 30° C to the original concentration of 9 per cent, and was then exposed a third time for 1 hour to electric discharges.

After the benzene had been distilled off, the iodine numbers and the softening temperatures of the soluble polymer and of the insoluble polymer from the second and third exposures were determined.

It can be seen from Table 6 that twice-repeated exposure to electric discharges did not increase the degree of polymerization. Thus, the iodine number of the soluble product remained practically as little changed as did that of the insoluble product. Evidently electric discharges increase the size of the original molecules, and when the latter reach a certain degree of polymerization they separate as an insoluble polymer. Repeated electric treatments do not therefore increase the molecular size appreciably above this point, but merely force the soluble polymers over the threshold of flocculation, beyond which point they are hardly in a condition to undergo any further essential change.

SYNTHETIC RUBBER (BUNA-85)

Nine per cent solutions of Buna-85 also were exposed in exactly the same way to repeated electric discharges; the insoluble deposit was separate each time, and the product remaining in solution was concentrated to its original strength. The experimental results were similar to those with natural rubber recorded in Table VI, and are summarized in Table VII. Like the previous tests, they show that in all cases polymerization in solution progressed only to a certain well

defined stage, beyond which point an increase in network formation of the molecules caused them to separate as a gel from the solution.

TABLE VI

REPEATED ELECTRIC TREATMENTS OF NATURAL RUBBER

	Softening temperature	Iodine number
Natural rubber (untreated)	135° C	362.0
Soluble polymer:		
From 1st treatment	145° C	248.0
From 2nd treatment	146° C	238.0
From 3rd treatment	145° C	246.2
Insoluble polymer:		
From 1st treatment	200° C	71.0
From 2nd treatment	200° C	71.0
From 3rd treatment	197° C	70.6

TABLE VII

REPEATED ELECTRIC TREATMENTS OF BUNA-85

	Softening temperature	Iodine number
Buna-85 (untreated)	150° C	316.2
Soluble polymer:		
From 1st treatment	164° C	230.0
From 2nd treatment	164° C	233.0
From 3rd treatment	165° C	233.0
Insoluble polymer:		
From 1st treatment	210° C	168.0
From 2nd treatment	210° C	170.5
From 3rd treatment	210° C	165.5

ATTEMPTS TO PREPARE MIXED POLYMERS OF NATURAL RUBBER AND OF BUNA-85 WITH NON-RUBBER SUBSTANCES

It seemed that it might be of importance to determine whether substances such as acrylic nitrile, $H_2C{:}CHCN$, combine with natural rubber under the influence of silent electric discharges, and as a consequence whether socalled mixed polymers might be prepared in this way.

A 10 per cent solution of acrylic nitrile in benzene was first studied in solution by itself. On exposure to electric discharges for 1 hour, there was a noticeable increase in viscosity, in spite of the fact that a part of the nitrile volatilized. The time of flow of the solution increased from 2.6 to 3.1 seconds.

A 6 per cent solution of purified natural rubber in benzene, containing also 1.2 per cent of acrylic nitrile (20 per cent by weight of the rubber), was exposed to electric discharges for 3 hours; the rubber was then precipitated by acetone, was extracted with acetone for 24 hours, and was dried in a vacuum (1 mm. of mercury) at 50° C. A determination of the nitrogen content by the Dumas method indicated no additional nitrogen in the product. Accordingly, under the particular conditions of the experiment, no acrylic nitrile combined with rubber. Nor did any acrylic nitrile combine Buna-85 under the same conditions.

To settle this problem satisfactorily, a considerable change, not contemplated at first, would obviously have had to be made in the experimental procedure.

TECHNOLOGICAL ASPECTS

As was pointed out in the introductory remarks, it seemed worthwhile to ascertain the technically important properties of the new polymeric types of rubber. Unfortunately however, only small quantities of the polymers were available for such work, so that a really systematic series of experiments to determine the most suitable vulcanizing agents and fillers and their best proportions could not be carried out. Starting with a few ordinary natural rubber mixtures of the tire-tread type, the work was limited to preparing and making comparative tests with very small quantities of the polymers. Under such conditions the most suitable choice or proportions of vulcanizing agents and other ingredients was of course not possible in every case. Nevertheless, the experiments give an indication of the technically important properties of the new types of rubber prepared from natural rubber and from Buna-85, and they prove that, at least from the technical point of view, the properties of natural rubber and of Buna-85 can be improved by exposure to electric discharges[18].

Rubber and Buna-85 mixtures were vulcanized in the form of sheets 3 mm. thick for 30, 60 and 90 minutes at 3 atmospheres' pressure, and from these, small normal test-specimens were cut out for obtaining stress-strain curves. Vulcanizates of the tire-tread type prepared from natural rubber and from polymers of natural rubber gave curves which were very similar to one another. When decalin was used as solvent, a part of it remained, probably in the form of a polymer, in the dried polymerized rubber. By increasing the percentage of sulfur, tensile strengths and elongations higher than the corresponding values for natural rubber vulcanizates were obtained, regardless whether these contained relatively high or low percentages of sulfur. In mixtures which contained, besides 10 per cent of zinc oxide, only the necessary vulcanizing agents, the polymers of Buna-85 showed properties superior to those of untreated Buna-85, *e. g.*, twice the tensile strength and almost 3 times the elongation at rupture. As was to be expected, the tensile strength was increased also by the addition of carbon black (to mixtures containing 2 per cent of sulfur by weight of the rubber). Here too, the quality of the vulcanizate containing polymerized Buna-85 was better than that containing untreated Buna-85. The actual measurements were as follows:

Product	Tensile strength (kg. per sq. cm.)	Elongation at rupture (percentage)
Buna-85	100	400
Polymerized Buna-85	142	390
Natural rubber (crepe)	184	400

The polymer prepared from Buna-85 therefore approached more nearly to natural rubber in mechanical properties.

By increasing the sulfur to 3.4 per cent (by weight of the rubber), the following values were obtained.

Product	Tensile strength (kg. per sq. cm.)	Elongation at rupture (percentage)
Buna-85	140	380
Polymerized Buna-85	194	420
Natural rubber (crepe)	200	300

A comparison on a technically sound basis would be possible only if a series of experiments were to be carried out with each type of rubber to determine the most favorable conditions, including the best choice and proportions of compound-

ing ingredients, the best time and temperature of vulcanization, etc. But to do this would have required the preparation of much larger quantities of the new types of rubber than were available in the experiments actually carried out in the present work. Nevertheless the experiments do give an indication of the way in which polymerization by electric discharges changes the properties of natural rubber and those of Buna-85 after vulcanization, and it does not seem unreasonable to hope for more important results through improvements in the method of polymerization and compounding of the polymers, and through a more thorough study of the technical aspects of the subject in general.

SUMMARY

The object of the investigation was to synthesize higher molecular compounds from natural rubber and from synthetic rubber by means of a process involving exposure to silent electric discharges. With both natural rubber and synthetic rubber, it was found possible to bring about polymerization by this method and to obtain polymers of various molecular sizes, which could be separated into two principal types: (1) polymers which remained soluble in benzene, and (2) polymers with a highly developed network structure, which were insoluble in benzene and therefore could be separated from the soluble polymers.

After purification and drying, the insoluble polymers were obtained as inelastic, nonplastic products, in the form of soft, crumbly flakes. On the contrary, the soluble polymers retained the plasticity and elasticity of the original rubber, and behaved like raw rubber in the technical sense as well. This latter fact was proved by preparing a few mixtures and vulcanizates from these polymers, and it is noteworthy that a vulcanizate prepared from polymerized Buna-85 more nearly resembled a corresponding vulcanizate from untreated natural rubber than it did a vulcanizate prepared from the original, untreated Buna-85. Of course more extensive development work would be necessary to obtain polymers with particularly desirable properties from a technical point of view, and to find out how to compound these new polymers, *e. g.*, what types and percentages of fillers, accelerators, and percentages of sulfur to use. Only in this way can the technical importance of these products be judged, and can any uses to which they may be applied to advantage be determined. But whatever may be their importance, the increased molecular sizes of these polymers of natural rubber and of Buna-85 are accompanied by marked increases in softening temperature without sacrifice of their technically important advantages of plasticity, tackiness and solubility. To this extent a not unimportant goal from the technical point of view may be regarded as having already been attained.

From the theoretical point of view, the formation of high molecular forms of rubber has been shown to be a polymerization process brought about by forced activation of the molecules. The course of the phenomenon is therefore governed by the electrical conditions, and is not greatly influenced by changes in temperature between $-25°$ and $50°$ C. Elementary analyses of the polymers showed in all cases the elementary formula of isoprene for the polymers of natural rubber, and of butadiene for the polymers of Buna-85.

From the chemical and physico-chemical points of view, the polymeric forms of rubber have characteristic degrees of unsaturation and consequently characteristic iodine numbers, both of which decrease with increase in the molecular size. Furthermore thermochemical measurements, comprising determinations of the heats of combustion in a microcalorimeter, showed that the polymerization reactions are exothermic, and that the heats of combustion of the resulting

polymers become smaller as the degree of polymerization increases. It was found possible, by measurements of the internal friction, to follow the progress of polymerization to the point where a gel separates.

REFERENCES

[1] The present paper is a thesis by Heinrich Leber at the University of Giessen.
[2] Berthelot and de Hemptinne, cf. bibliography in Stähler, "Handbuch der Arbeitsmethoden in der anorganischen Chemie", Berlin, **1925.**
[3] Hock, *Z. Electrochem.* **29**, 111 (1923).
[4] Eichwald and Vogel, *Z. Angew, Chem.* **35**, 505 (1922); **36**, 611 (1923).
[5] Becker, *Wiss. Veröffentlichungen Siemens-Konzern* **5**, 160 (1926); **8**, 199 (1929).
[6] Hock and Nottebohm, *Kolloidchem. Beih.* **31**, Nos. 6-8, (1930).
[7] Hock and Fromandi, *Kolloidchem. Beih.* **26**, 189 (1928).
[8] The sulfur bridges of Hock ("Handbuch Kautschukwissenschaft", Leipzig, **1930**, p. 480) and of Meyer and Mark ("Der Aufbau der hochpolymeren organischen Naturstoffe", Leipzig, **1930**).
[9] Mark and Raff, *Z. physik. Chem.* **31B**, 275.
[10] Schulz and Husemann, *Z. physik. Chem.* **176A**, 317.
[11] Staudinger and Dreher, *Ber.* **69**, 1729 (1936).
[12] These samples of rubber were kindly furnished by Dr. Konrad of the I. G. Farbenindustrie A. G., Leverkusen.
[13] The authors are grateful to Hermann Schmidt for his help in the preparation of larger quantities of experimental material.
[14] Kautsky and Thiele, *Z. anorg. allgem. Chem.* **152**, 344 (1926).
[15] Kemp, *India-Rubber J.*, May 28, **1927**; see also Fromandi, *Kolloidchem. Beih.* **37**, 212 (1928).
[16] Geiger, Thesis No. **422**, Technische Hochschule, Zurich, **1926**, p. 31.
[17] The U. S. Bureau of Standards obtained a value of 10.82×10^3 calories for highly purified rubber. In the present work only the heat of combustion of natural rubber reprecipitated once by acetone is concerned, since the only question was the change in the heat of combustion as a result of polymerization.
[18] The authors wish to express their thanks to Dr. Konrad of the I. G. Farbenindustrie A. G., Leverkusen, for his friendly aid in preparing the necessary quantities of soluble polymer from large volumes of solvent by careful distillation in a vacuum, and to Dr. Grähling of the Deutsche Dunlop Gummi-Compagnie A. G., Hanau, for carrying out the experiments with technical mixings.

DESTRUCTIVE HYDROGENATION OF HIGH-MOLECULAR-WEIGHT POLYMERS

ISOBUTENE POLYMER, BUTADIENE POLYMER, AND NATURAL RUBBER *

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Destructive hydrogenation under pressure in the presence of nickel oxide and molybdenum oxide has been used to show the presence of naphthenic hydrocarbons in high-boiling olefin polymer[2]. It was of interest to apply this tool to other hydrocarbons having large molecules, especially rubber and synthetic rubber like polymers.

The destructive hydrogenation of isobutene polymer yielded only paraffinic hydrocarbons, including isobutane in the gases. Butadiene polymer, on the other hand, gave only naphthenic products, chiefly ethylcyclohexane and a dicyclic hydrocarbon. Similarly, natural rubber yielded only naphthenes, with *p*-methylisopropylcyclohexane as the major component of the lower boiling portion of the product. Isoprene, under the conditions used for the destructive hydrogenation of the rubber, yielded isopentane and an unsaturated naphthene, *i. e.*, a hydropolymer of isoprene, which was converted into *p*-methylisopropylcyclohexane by further hydrogenation.

Discussion of the relation of these results to the structures of the polymeric substances hydrogenated is reserved for a future publication of further work now in progress undertaken to aid in the proper interpretation of the above indicated experiments.

APPARATUS AND PROCEDURE

The destructive hydrogenations were carried out in electrically heated, rotating autoclaves (450- and 3515-cc. capacity) of the Ipatieff type, made of stainless steel (17-19 per cent chromium and 7.0-9.5 per cent nickel). Equal weights of the rubberlike polymer or rubber (cut into small pieces) and solvent, and black nickel oxide (Baker's), equivalent to 10 per cent of the weight of the polymer, were placed in the autoclave in the order named. The autoclave was closed, the air was swept from it by hydrogen, and it was charged with hydrogen to an initial pressure of 100 kg. per sq. cm. at 25° C, and then heated at 250° for 4 to 12 hours (an additional 1.5 to 2.0 hours usually being required to reach the desired operating temperature). After the heating, the autoclave was permitted to cool, the gases were released through a trap cooled by solid carbon dioxide and acetone, and the noncondensable gases were collected in a gas holder over salt water. The head was then removed from the autoclave, and the liquid product and solvent were taken from the bomb by means of a pipet and filtered to remove the catalyst. The solvent was removed and the product was separated by fractional distillation.

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DESTRUCTIVE HYDROGENATION OF ISOBUTENE POLYMER IN PRESENCE OF BLACK NICKEL OXIDE

The white rubberlike polymer which was hydrogenated destructively in this work was obtained by polymerizing isobutene in liquid propane solution in the presence of aluminum chloride and hydrogen chloride. For example, 10 grams of resublimed anhydrous aluminum chloride were covered by liquid propane in a 500-cc. three-neck flask fitted with a motor-driven stirrer and surrounded by a bath of solid carbon dioxide and acetone at −78° C. Temperatures within the flask were measured by a thermocouple inserted in a glass well, which extended almost to the bottom of the flask. Then 230 cc. of a solution of 21.5 mole-per cent of isobutene in propane and 1.5 grams of gaseous hydrogen chloride were added gradually during a period of 1.5 hours to the stirred mixture of aluminum chloride and propane, maintained at approximately −75° C. After all the isobutene-propane solution was added, the total propane solution, later found to contain 8.5 mole-per cent isobutene and 3.2 grams of heavy oil, was decanted from a gummy product and from admixed aluminum chloride, which had become slightly yellow during use. Then ice-water and cold ammonium hydroxide solution, added carefully to the aluminum chloride residue and gummy product, decomposed the aluminum chloride and left 12.6 grams of white rubberlike polymer material of the nature of that formed in larger scale polymerizations and used as starting material in the present destructive hydrogenation tests.

This white rubberlike polymer was cut into small pieces and hydrogenated by the above procedure, using 100 cc. of *n*-pentane as solvent with 50 grams of the rubberlike polymer. Gases condensable at −78° C, totaling 44 per cent by weight of the polymer charged and the noncondensable gases (2.5 weight per cent), had the following analyses:

Condensable gas (mole-%)		Noncondensable gas (mole-%)	
Propene	0.3	Olefins (total by Br)	0.1
Propane	7.9	Oxygen	0.9
Isobutene	0.0	CO	0.0
n-Butene	0.9	Hydrogen	84.0
Isobutane	73.4	Paraffins	9.3
n-Pentane (the solvent)	17.5	Nitrogen	5.7
		Index of paraffins	1.67

After removal of the solvent, the liquid products were distilled by the high-temperature Podbielniak method[4], and separated into fractions with the properties shown in Table I. The analyses and properties indicate that fraction 1 consists of octanes, fraction 4 of dodecanes, fractions 5 and 6 of hexadecanes, and the bottoms of hydrocarbons with an approximate formula $C_{44}H_{90}$ (molecular weight 618). According to these analyses and properties, these products are entirely paraffinic.

DESTRUCTIVE HYDROGENATION OF BUTADIENE THERMAL RUBBER

Rubberlike polymers formed by heating butadiene at 150° C under 40 atmospheres' initial pressure and freed by vacuum distillation from oils boiling below 300° C were subjected to destructive hydrogenation. A test at 100° C caused no decomposition, but during 6 hours at 250° C part of the rubbery polymers was converted into liquid products which were stable to nitrating mixture. The residue of undecomposed polymers was more stable than the original polymer, as 11.0 grams of this residue yielded only 1 cc. of liquid products

TABLE I

DESTRUCTIVELY HYDROGENATED ISOBUTENE POLYMER

Fraction no.	Boiling range		Dist. % by wt. per fraction	n_D^{20}	d_4^{20}	Mol. wt.	Analysis, %			
							Found		Calcd. for C_nH_{2n+2}	
	° C (mm. Hg)	° C (760 mm.)					C	H	C	H
1	102-126 (750)	—	19.0	1.3970	0.7030	117	84.00	15.65	84.24	15.76
2	126-149 (750)	—	7.8	1.4058	0.7231	123	84.45	15.44	—	—
3	50-75 (10)	166-197	10.0	1.4278	—	—	85.05	15.12	—	—
4	75-95 (10)	197-222	2.1	1.4270	0.7730	174	84.80	14.98	84.60	15.40
5	95-125 (11)	222-258	5.8	1.4438	0.7925	200	84.80	15.05	84.80	15.20
6	125-151 (10)	258-293	4.0	1.4461	0.8110	242	84.90	14.96	—	—
Bottoms	—	—	51.3	—	0.8744	625	85.04	14.62	85.40	14.60

after further destructive hydrogenation for 8 hours at 240-250° C under 100 kg. per sq. cm. hydrogen pressure in the presence of 1 gram of black nickel oxide. Distillation of the total liquid products obtained at 250° C gave the fractions with properties indicated in Table II.

Fractions 2 and 3, which had the physical properties of ethylcyclohexane, were combined and dehydrogenated over platinized alumina at 250° C. The 3.8 cc. of

Autoclave assembly used in destructive hydrogenation (furnace top removed to show autoclave).

TABLE II

DESTRUCTIVELY HYDROGENATED BUTADIENE POLYMER

Fraction no.	Boiling range at 750 mm. (° C)	Dist. vol.-% per fraction	n_D^{20}
1	124-130	9.6	1.4083
2	130-135	23.7	1.4325
3	135-145	25.7	1.4367
4	145-230	9.6	1.4617
5	230-295	11.4	1.4771
6[a]	295-310	7.1	1.4605
Bottoms	—	11.9	1.4850

[a] Per cent analysis: found, C 86.20, H 13.81; calculated for $C_{16}H_{30}$, C 86.40, H 13.60.

composite with n_D^{20} of 1.4350 yielded 3.7 cc. of dehydrogenation product, with n_D^{20} of 1.4403, and 735 cc. of gas analyzing 97 per cent hydrogen. The dehydrogenated liquid was converted into a diacetamino derivative[3], melting at 224-225° C, and corresponding to that of ethylbenzene formed from ethylcyclohexane, a product of the destructive hydrogenation of the rubbery butadiene polymer.

Fraction 6 was saturated, as shown by its stability to both potassium permanganate solution and to nitrating mixture. Its analysis corresponded to that of a naphthenic hydrocarbon with two rings. These results show the products from the destructive hydrogenation of butadiene rubber to be naphthenic hydrocarbons with one or two rings.

DESTRUCTIVE HYDROGENATION OF RUBBER IN PRESENCE OF BLACK NICKEL OXIDE

Both smoked sheet and pale crepe rubber yielded similar unsaturated destructive hydrogenation products containing 40 to 50 per cent of liquids boiling below 300° C. The remainder consisted of higher boiling liquid or viscous products. After removal of the cyclohexane solvent, the product obtained from pale crepe rubber was separated by high-temperature Podbielniak distillation into fractions with the properties shown in Table III. No isopentane was detected in the solvent removed from any of these destructive hydrogenation products of rubber.

Destructive hydrogenation products of both pale crepe and smoked sheet rubber were hydrogenated to completion at low temperatures (up to 150° C) in the presence of a nickelkieselguhr catalyst[1], with the results listed in Table IV. These data show that only naphthenic and polycyclic hydrocarbons were formed by the destructive hydrogenation of rubber.

The completely hydrogenated fraction with 167-170° C boiling range, obtained from the destructive hydrogenation products of both smoked sheet and pale crepe rubber, had a density, refractive index, molecular weight, and carbon and hydrogen content in complete agreement with the best values reported in the literature for these properties of *p*-methylisopropylcyclohexane (*p*-menthane).

Further proof of the presence of *p*-methylisopropylcyclohexane in the products from both smoked sheet and pale crepe rubber was obtained by dehydrogenating the 167-190° C fractions at 250° C over platinum supported by activated alumina. The gases obtained consisted of 96 per cent hydrogen. After dehydrogenation, the liquid products were brominated at room temperature in the presence of aluminum powder and iodine, and yielded white needles which, after recrystallization from benzene, had a melting point of 276-278° C. These crystals were the same as those obtained similarly from *p*-cymene or from the dehydrogenation product formed from completely hydrogenated dipentene; the latter had a boiling point of 169-170° C, and n_D^{20} of 1.4402. These crystals were pentabromotoluene, formed by cleavage of an isopropyl group from *p*-cymene during the bromination. Analysis of this bromide was as follows: Calculated for $CH_3C_6Br_5$: Br, 82.0; molecular weight, 487. Calculated for $CH_3C_6Br_4$ (iso-C_3H_7): Br, 71.2; molecular weight, 450. Found: Br, 80.58, 81.15; molecular weight, 505.

Further evidence of *p*-cymene in these dehydrogenation products was the *p*-toluic acid (melting point 177-179° C) formed by oxidation with dilute nitric acid (1.0 cc. hydrocarbon refluxed for 12 hours with 15 cc. of concentrated nitric acid in 25 cc. of water). Accordingly it is concluded that the completely hydrogenated 167-190° C fraction obtained from rubber contained *p*-methylisopropylcyclohexane.

HYDROGENATION OF ISOPRENE

Isoprene in cyclohexane under 100 atmospheres of hydrogen pressure at 250° C, in the presence of 10 per cent by weight of black nickel oxide, yielded 32 per cent by weight of isopentane and 68 per cent of hydropolymerized isoprene boiling from 155° to 190° C, as indicated in Table V.

Redistillation of fraction 1 by the low-temperature Podbielniak method[5] showed it to contain 7.6 per cent of butanes and 92.4 per cent of isopentane. The liquid products boiling from 155° to 190° C were unsaturated, and consisted of incompletely hydrogenated isoprene dimers, which were converted into methane by further hydrogenation.

TABLE III

DESTRUCTIVELY HYDROGENATED PALE CREPE RUBBER

Fraction no.	Boiling range °C	Boiling range Mm. Hg	Normal B. P. (° C)	Dist. vol.-% per fraction	n_D^{20}	d_4^{20}	Br. no.	Analysis found, % C	Analysis found, % H
1	97-110	747	—	2.4	1.4258	—	—	—	—
2	110-127	747	—	2.1	1.4335	0.7723	49	86.26	13.68
3	127-156	747	—	3.8	1.4410	0.7847	51	—	—
4	156-163	747	—	3.7	1.4463	0.8013	53	86.29	13.44
5	163-171	747	—	7.2	1.4520	0.8119	54	86.86	12.87
6	171-182	747	—	8.9	1.4598	—	—	—	—
7	182-193	747	—	1.3	1.4662	—	—	—	—
8	60-67	8	182-192	8.9	1.4771	—	—	—	—
9	67-88	8	192-217	7.1	1.4864	—	—	—	—
10	88-93	1	217-270	3.7	1.4950	—	—	—	—
11	93-115	1	270-301	3.8	1.4977	—	73	—	—
12	115-143	6	301-293	6.3	1.5043	—	59	—	—
Bottoms (black, viscous)			Decomp.	40.8	(by difference)		—	—	—

TABLE IV

PROPERTIES OF COMPLETELY HYDROGENATED PRODUCTS FROM DESTRUCTIVE HYDROGENATION OF RUBBER

Product from	Boiling range ° C (mm. Hg)	Boiling range ° C (760 mm.)	n_D^{20}	d_4^{20}	Mol. wt.	Analysis, % Found C	Found H	Formula	Calcd. C	Calcd. H
Crepe	125-155 (751)	—	1.4251	0.7602	112	85.23	14.47	C_8H_{16}	85.65	14.35
Sheet	167-169.5 (744)	—	1.4402	0.7993	143	85.43	14.51	$C_{10}H_{20}$	85.65	14.35
Crepe	171-190 (750)	—	1.4449	0.8109	146	85.69	14.35	$C_{10}H_{20}$	85.65	14.35
Crepe	90-100 (0.6)	277-290	1.4786	0.8832	234	86.87	13.10	$C_{17}H_{30}$	87.05	12.95
Sheet	149-160 (1.0)	343-356	1.4859	0.8957	335	85.88	13.04	$C_{25}H_{44}$	87.10	12.90

TABLE V

PRODUCTS FROM HYDROGENATION OF ISOPRENE IN CYCLOHEXANE SOLUTION

Fraction no.	Boiling point (° C)	Dist. % by wt. of total product and solvent	n_D^{20}
1	29-31	16.5	—
2	31-155	55.0	—
3	155-166	4.0	1.4447
4[a]	166-175	8.6	1.4500
5	175-190	3.2	1.4529
Bottoms	—	7.0	1.4739

[a] d_4^{20}, 0.8099; mol. wt., 143. Per cent analysis: found, C 86.51, H 13.55; calculated for $C_{10}H_{18}$, C 86.8, H 13.2.

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REFERENCES

[1] Ipatieff and Corson, *Ind. Eng. Chem.* **30**, 1039 (1938).
[2] Ipatieff and Pines, *J. Org. Chem.* **1**, 464 (1936).
[3] Ipatieff and Schmerling, *J. Am. Chem. Soc.* **59**, 1056 (1937).
[4] Podbielniak, *Ind. Eng. Chem., Anal. Ed.* **5**, 119, 135 (1933).
[5] *Ind. Eng. Chem.* **5**, 172 (1933).

SYNTHETIC RUBBER FROM ACETYLENE

III. THE PREPARATION OF BUTADIENE BY CATALYTIC HYDROGENATION OF MONOVINYLACETYLENE IN THE GASEOUS PHASE *

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Of the various technical methods for the preparation of butadiene from monovinylacetylene, the present authors chose to make first of all a thorough investigation of the continuous hydrogenation process, utilizing gaseous monovinylacetylene with various catalysts. As a result of this work the following conclusions were reached.

The chief fault of this continuous hydrogenation process lies in the fact that, in addition to butadiene, large quantities of butene and oily polymerization products of monovinylacetylene are formed, as a result of which the yield of butadiene is small. This disadvantageous course of the reaction is attributable

TABLE I

INFLUENCE OF THE TEMPERATURE OF REACTION

(Catalyst = palladium-diatomaceous earth 1:1028; 2 grams; velocity of current = 110 cc. per min.)

Reaction temperature ° C	Reaction products (Molecular-percentage yield based on monovinylacetylene)			
	Unconsumed monovinylacetylene	Butadiene	Butene	Oily polymerization products
19	86.6	8.5	—	4.9
32	29.2	22.4	17.1	31.3
44.5	19.7	29.2	21.4	29.7
61.5	23.1	27.2	24.8	24.9
100	16.8	24.6	24.8	33.8
100	11.8	30.1	26.1	32.0

to the great heat of reaction which is evolved locally on the surface of the catalyst. In the experiments carried out by the present authors, the chief efforts were directed toward overcoming this drawback.

As may be seen in Table II, a series of experiments were carried out with palladium as catalyst, which was used with excess carrier having a low heat conductivity, *e. g.*, diatomaceous earth and Japanese acidic earth. This catalyst was expected to have a weakening effect on the activity, for this effect is very pronounced in the hydrogenation of acetylene to ethylene. In the present case, however, the results were unsatisfactory; dilution of the reaction gas with water vapor, a change in the gas current, and a change in the proportion of hydrogen to monovinylacetylene, were all tried. The maximum yield of butadiene at 80° C was 33.7 per cent, based on the monovinylacetylene.

Nickel, cobalt and iron, to which diatomaceous earth had been added, were less effective than palladium. Raney nickel was too active, and led to carbonization of the monovinylacetylene.

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Experiments with a few palladium catalysts, which, to remove the great quantity of heat of reaction evolved, were prepared on metal powders or metal

TABLE II

INFLUENCE OF THE QUANTITY OF CARRIER

(Reaction temperature 80° C)

Catalyst (Palladium-diatomaceous earth)	Unconsumed monovinyl-acetylene	Butadiene	Butene	Oily polymerization products
1:50	21.6	25.4	24.2	28.8
1:100	21.4	27.0	22.6	29.0
1:403	13.0	27.2	28.0	31.8
1:609	22.3	25.8	28.7	22.0
1:1028	16.6	30.6	28.7	23.1
1:1350	16.1	24.5	28.7	31.2
1:2021	17.5	27.1	28.7	26.7
1:4060	27.8	30.1	21.3	20.8

TABLE III

EXPERIMENTS WITH VARIOUS GASEOUS MIXTURES

(Catalyst = palladium-diatomaceous earth 1:1028; 2 grams; velocity of current 110 cc. per min.)

Ratio monovinylacetylene / hydrogen	Reaction temperature (° C)	Reaction products (Molecular percentage yield (based on monovinylacetylene))			
		Unconsumed monovinyl-acetylene	Butadiene	Butene	Oily polymeri-zation products
1:2.43	81.5	2.44	3.2	69.7	24.7
1:1.92	81.0-82.0	6.1	18.4	60.4	15.1
1:1.20	80.0	16.6	30.6	28.7	23.1
1:0.46	78-79	58.4	15.4	9.06	17.1
With water vapor saturated at 43° C	80	8.6	33.7	30.4	27.3
With water vapor saturated at 61° C	80	17.3	25.3	34.9	22.5

TABLE IV

INFLUENCE OF THE VELOCITY OF CURRENT

(Catalyst = palladium-diatomaceous earth 1:1028)

Velocity of current (cc. per min.)	Weight of catalyst (g.)	Reaction tempera-ture (° C)	Reaction products (Molecular percentage yield, based on monovinylacetylene)			
			Unconsumed monovinyl-acetylene	Butadiene	Butene	Oily polymeri-zation products
56	2	80	21.7	28.0	26.0	24.3
110	2	80	20.3	28.2	25.1	25.9
185	2	80	25.6	25.3	25.7	22.8
200	1	82	26.8	24.2	24.7	24.3
510	1	80	33.3	22.6	22.7	18.2

turnings (*cf.* Karo, German patent 253,160 (1912)), showed that this method is particularly advantageous. With palladium catalyst on magnesium turnings and excess hydrogen, the yield of butadiene was 32 per cent, *i. e.*, 49 per cent of

the monovinylacetylene consumed. In this case the quantity of butene was one-half that of the butadiene.

Palladium-iron-diatomaceous earth was the best among the mixed catalysts tested. Yet even in this case a large quantity of oily byproducts was formed, as was the case with palladium-nickel-diatomaceous earth.

TABLE V

EXPERIMENTS WITH NICKEL, COBALT AND IRON CATALYSTS

(Velocity of current 110 cc. per min.)

Catalyst	Reaction temperature (° C)	Reaction products (Molecular percentage, based on monovinylacetylene) Unconsumed monovinylacetylene	Butadiene	Butene	Oily polymerization products
Nickel-diatomaceous earth (1:50) 1 g....	150	34.0	3.2	12.0	39.5 (11.3 butane)
Raney nickel 6 g.....	85	carbonized	..	...	...
Cobalt-diatomaceous earth (1:50)	140, 270	no reaction	..	...	...
Cobalt-diatomaceous earth (1:1)	80-90	52.3	4.7	15.1	27.9
Iron-diatomaceous earth (1:1)1 g.....	200	76.8	7.2	5.7	10.3
Iron-diatomaceous earth (1:1) 1 g.....	300	72.2	2.2	7.8	17.8

IV. THE PREPARATION OF BUTADIENE BY CATALYTIC HYDROGENATION OF MONOVINYLACETYLENE IN SOLUTION

ZYUNZI HURUKAWA and TADASI TUKAMOTO

In the work described in the present paper, experiments were carried out on the catalytic hydrogenation of monovinylacetylene to butadiene in solution, with the same aim in view as that in the previous experiments (see Part III).

In general the results of these latest experiments were more favorable than those with monovinylacetylene in the gaseous phase, for in solution it is somewhat easier to remove the heat of reaction which is evolved locally on the surface of the catalyst.

A large number of experiments with various catalysts and with several solvents was carried out, and it was found that the best results were to be obtained with palladium black or with palladium-diatomaceous earth in ethyl acetate. It was also found that when the reaction is carried out under pressure, a concentrated solution of monovinylacetylene or monovinylacetylene alone without a solvent can be used; however, not only is this of no particular advantage, but it actually increases the proportion of byproducts, *i. e.*, the proportions of butene and oily products. In this case the increase in the temperature of the reaction is considerable unless provision is made for cooling of the apparatus.

The quantity of catalyst carrier in relation to that of the catalyst itself has no great effect on the yield of butadiene. In the experiment with palladium black, *i. e.*, in the absence of a carrier, there was a tendency for the yield of polymerization products to increase.

TABLE VI

EXPERIMENTS WITH PALLADIUM CATALYSTS DEPOSITED ON METALS

Catalyst	Reaction temperature (° C)	Current velocity (cc. per min.)	Reaction products: Unconsumed monovinylacetylene	Butadiene	Butene	Oily polymerization products
Palladium-aluminum (1:100) 1 g.	75-85	110	39.2	12.2	34.7	13.9
Palladium-aluminum (1:1000) 2 g.	85	77	26.0	19.6	17.6	36.8
Palladium-copper (1:100)	90, 160	110	no reaction		...	...
Palladium-magnesium (1:10) 1 g.	66	110	44.2	15.6	29.6	10.6
Palladium-magnesium (1:1000) 4 g.	85	110	36.9	16.3	22.3	24.5
Palladium-magnesium (1:4000) 8 g.	85	110	72.5	3.1	11.8	12.6
Palladium-magnesium (turnings) 0.8 g.	70	19	34.6	32.2	12.8	20.4
Palladium-magnesium (turnings) 2 g.	70	38.5	33.7	32.6	16.1	17.6
Palladium-magnesium (turnings) 2 g.	143	110	19.6	28.2	26.8	25.4

TABLE VII

EXPERIMENTS WITH MIXED PALLADIUM CATALYSTS

Catalyst	Reaction temperature (° C)	Current velocity (cc. per min.)	Unconsumed monovinylacetylene	Butadiene	Butene	Oily polymerization products
Palladium-nickel-diatomaceous earth (1:5:1000).	77-81.5	110	13.4	8.9	15.7	62.0
Palladium-nickel-diatomaceous earth (1:5:1000).	58	110	30.6	14.7	20.9	33.8
Palladium-nickel-diatomaceous earth (1:50:5000).	70	110	94.1	2.6	...	3.3
Palladium-iron-diatomaceous earth (1:10:100).	54-60	77	9.0	19.0	18.5	53.4
Palladium-iron-diatomaceous earth (1:100:100).	122-125	77	9.1	25.1	26.8	34.9
Palladium-iron-diatomaceous earth (1:100:1000).	170-180	77	18.4	19.4	15.3	46.9
Palladium-iron-diatomaceous earth (1:1000:1000).	215-220	77	21.3	23.6	14.4	40.7

In general the reaction did not seem to proceed stepwise. Even at the beginning of the reaction, rather large quantities of butene and polymerization products were formed. As may be seen in Figure 1, the yield of butene was a maximum when the reaction was stopped at the point at which 120-130 per cent of the theoretical quantity of hydrogen (65 per cent based on the monovinylacetylene) had been absorbed.

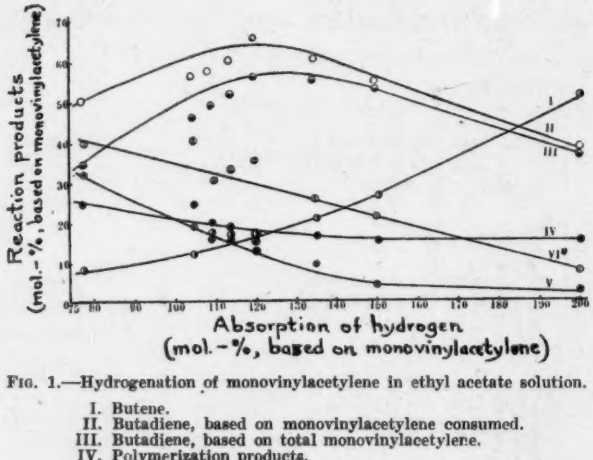

FIG. 1.—Hydrogenation of monovinylacetylene in ethyl acetate solution.

I. Butene.
II. Butadiene, based on monovinylacetylene consumed.
III. Butadiene, based on total monovinylacetylene.
IV. Polymerization products.
V. Monovinylacetylene unconsumed.
VI. Ratio: butadiene: butene.

The reaction was found to proceed very satisfactorily at 5-20° C; above 20° C the yield of byproducts increased.

The influence of the proportion of catalyst was investigated. A large proportion of catalyst increased the velocity of the reaction; at the same time, however, there was a greater tendency to form byproducts. This same tendency was evident when the proportion of catalyst was too small.

The experiments show that the drawback of the process lies in the formation of byproducts in considerable quantities. This point must be given special consideration from the technical point of view.

SYNTHETIC RUBBERS: A REVIEW OF THEIR COMPOSITIONS, PROPERTIES, AND USES *

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I. INTRODUCTION

Synthetic rubber has been the dream of many during the century which has passed since Faraday first determined the carbon-hydrogen ratio in natural rubber, but it has completed only about a decade of commercial success. Every year of the past ten has seen an increase in the quantity produced, the number of varieties available, and the number of applications.

The aims in various countries have been different, and the development has proceeded in different directions. The most active research has been carried on in Germany, Russia, and the United States. There has been relatively little collection and intercomparison of the rather limited data on the physical properties of the different varieties of synthetic rubber. Scientific articles have been largely devoted to descriptions of single varieties or to discussions of limited phases of the work with respect to one variety. The present paper represents an attempt to make a summary of the facts regarding the different varieties, an intercomparison of some of their properties, as reported in previous publications, and to present a fairly complete bibliography of the modern literature on the subject of synthetic rubber. Because of the relatively short time during which the different varieties of synthetic rubber have been available, the data concerning them have been reported almost entirely by observers in the laboratories of companies each interested in the manufacture and sale of a particular variety. In almost every case, therefore, the figures necessarily lack independent confirmation.

The development of synthetic materials to replace those of vegetable or animal origin has been a matter of frequent occurrence. Many examples can be cited, beginning with alizarin and indigo, and continuing with dyes, fertilizers, drugs, and vitamins. Usually the development follows a fairly well-defined pattern, consisting of: (1) scientific research on the analysis of the natural product, leading to an exact knowledge of the chemical constitution and structure; (2) evolution of methods for the duplication of the substance from cheap raw materials, and (3) commercial production of the synthetic product at a price low enough to compete with, and even to displace, the natural product. In most cases the synthetic product is chemically and physically the same as the natural product and is not an improvement, unless the absence of impurities or nonessential ingredients can be considered an improvement.

Although thirty years ago the expectation was general that the development of synthetic rubber would follow this course, it has not done so, since serious difficulties were encountered with each of the three steps of the typical pattern of development. Consequently, scientific workers engaged in much research which now seems fruitless. The belief that the development should follow the customary pattern, as outlined, has given rise to many popular misconceptions as to the present status of synthetic rubber.

* A reprint of Circular of the National Bureau of Standards C 427; Issued June 25, 1940; 29 pages.

Scientific research on natural rubber has yielded much information, but even today it cannot be said that the structure of rubber is known in the sense that the structures of most substances of lower molecular weight are known. Our knowledge, though incomplete, is probably sufficient to enable us to say that no process has yet been found by which it is possible to produce a material possessing both the chemical constitution and the physical properties of natural rubber. Finally, the cost of the synthetic products which most nearly approach natural rubber in character is far above the present price of natural rubber. In view of these facts the whole approach to the problem has been revised. It seems now to be recognized that the desirable physical properties of rubber are not necessarily closely related to its chemical constitution, and since, in almost all its uses, its physical properties are of first importance, the effort to duplicate the chemical constitution of natural rubber has been abandoned.

In recent years the very meaning of the term "synthetic rubber" seems to have changed to agree with the change in the point of view. Thirty years ago, the term meant a synthetic material physically and chemically indistinguishable from natural rubber (except possibly for the absence of impurities). Since no material has been produced which fits this definition, the term has come to mean to most people a synthetic material possessing the approximate physical properties of natural rubber[224]. Several authors[4, 18, 19, 21, 225] have attempted to express such a definition in more exact terms. Others, following the older definition, have hesitated to use the phrase "synthetic rubber", and have taken refuge in the more indirect expressions "synthetic rubberlike material", "elastic synthetic", and "rubber substitute". Perhaps the most satisfactory solution would be the adoption of some single word such as "elastomer", as suggested by Fisher[7], but as yet no such word has met with general acceptance. The term "synthetic rubber" has been used so widely that it would probably be difficult to displace it.

The economic factors involved in the production of synthetic rubber have changed considerably in the past thirty years. The growth of plantation rubber in the Far East has reduced the price of natural rubber from the maximum of about $3 per pound in 1910 to less than 20 cents per pound in 1940. The cheapest commercial synthetic rubber still costs about twice as much as the natural product. Nevertheless, in recent years certain countries, notably Germany and Russia, insisting on economic self-sufficiency, have considered a high price paid within the country to be of little importance compared with expenditures in foreign currency for natural rubber. Self-sufficiency in wartime, of course, has also been a factor of paramount interest to these governments[14, 125].

These economic and political factors have influenced scientific objectives and development in the different countries. In Germany and Russia, the primary aim appears to have been to duplicate, or nearly duplicate, the properties of natural rubber as cheaply as possible and any improvement in qualities seems to have been of only incidental or secondary importance. In the United States, on the contrary, the primary aim has been to produce a product superior to natural rubber in some respect, the cost being a matter of secondary importance. In a free world market, only a superior synthetic rubber can justify a higher price. Whether or not in the future the other countries, including the United States, will be moved by considerations of self-sufficiency to follow Germany and Russia remains to be seen. Up to the present time, such considerations have not played much part in the development of synthetic rubber in these countries.

II. VARIETIES OF SYNTHETIC RUBBER

In conformity with the trend already mentioned, the term "synthetic rubber" in this paper will be taken to mean merely a synthetic substance which has physical properties resembling those of natural rubber; that is, it can be stretched a considerable amount, let us say to an elongation of at least 300 per cent, and when released will quickly and forcibly retract to substantially its original dimensions. About 30 varieties of synthetic rubber are listed in Table I, under the trade names used by the manufacturers. Of these, some are practically identical and some are very closely related to others. They have been classified in six general types, according to chemical composition, and the discussion in the present paper follows this classification. The chemical constitutions of almost all of the varieties in Table I, together with that of natural rubber, are shown in Table II.

In common with natural rubber, all types of synthetic rubber consist of atomic chains of very great length—giant molecules as they are sometimes called—built up by the repetition, usually thousands of times, of some unit configuration. In all but the last two cases shown in Table II, the long chains are built up by polymerization, or linking together, of the molecules of liquids. In the process of formation of the polymer from the liquid monomer, in each case the double bond attached to a carbon atom at the end of the molecule opens to form the necessary valence bond for attachment to the next unit. The organic polysulfide rubbers, which are illustrated by the last two types in Table II, possess long chains formed not by polymerization, but by condensation. The atoms at the ends of two different molecules combine with each other, thus leaving the remaining radicals free to combine, and forming long chains by the repetition of the process[180]. In none of the different varieties of synthetic rubber has the nature of the terminal group of the chain been definitely established. It comprises only a very small fraction of the total material, and may be different in different chains of the same material.

The production of synthetic rubbers involves two steps—the manufacture of the monomer, and the polymerization or condensation reaction. The first step usually follows fairly common and well-understood reactions; the second step is much more empirical and less understood, but usually involves the use of a catalyst and the control of temperature and pressure.

One of the most important improvements during the past few years has been the adoption, in many cases, of polymerization in emulsion. The monomer is emulsified in a liquid, usually water, and the product is a suspension similar to the latex of natural rubber. Another important advance was the discovery and development of copolymerization. This is a process involving the simultaneous polymerization of two or more liquids, and yielding a product in which a single chain contains units of both configurations. The copolymers of butadiene with styrene and of butadiene with acrylonitrile are the best known examples.

Prolonged research[28] has failed to locate a cheap source of supply for the manufacture of isoprene, or to produce from it a polymer with physical properties close to those of natural rubber. Consequently, efforts in these directions have been almost completely abandoned, and all the commercial synthetic rubbers differ chemically from natural rubber. Between 1915 and 1918, the Bayer plant in Germany produced about 2,500 tons of rubber from dimethylbutadiene[33]. The product, called "methyl rubber", has not, since then, retained any commercial importance. With these exceptions and possibly a few others, all

TABLE I

VARIETIES OF SYNTHETIC RUBBER

Name	Type	Remarks	Reference	Manufacturer	Country of origin
Buna 85	Butadiene polymer	Molecular weight about 85,000.	128	I. G. Farbenindustrie	Germany.
Buna 115	Butadiene polymer	Molecular weight about 115,000.	128	I. G. Farbenindustrie	Germany.
Buna N*	Butadiene copolymer	Copolymer with acrylonitrile; now called Perbunan.	128	I. G. Farbenindustrie	Germany.
Buna S	Butadiene copolymer	Copolymer with styrene	128	I. G. Farbenindustrie	Germany.
Buna SS	Butadiene copolymer	Copolymer with styrene—higher styrene content than Buna S.	129	I. G. Farbenindustrie	Germany.
Duprene*	Chloroprene polymer	Now called Neoprene	60	E. I. du Pont de Nemours & Co.	United States.
Ethanite	Organic polysulfide	Similar to Thiokol A	171, 182	Belgian Cracking Co.	Belgium.
Flamenol	Plasticized vinyl chloride polymer		...	General Electric Co.	United States.
Ker	Butadiene polymer		126	Stomil Co.	Poland.
Korogel	Plasticized vinyl chloride polymer	Highly plasticized Koroseal.	210	B. F. Goodrich Co.	United States.
Koroseal	Plasticized vinyl chloride polymer		212	B. F. Goodrich Co.	United States.
Levulkan*	Botadiene copolymer	Now called Buna SS	129	I. G. Farbenindustrie	Germany.
Methyl rubber B	Dimethylbutadiene polymer	Sodium used as catalyst	33	Bayer & Co., 1915-18	Germany.
Methyl rubber H	Dimethylbutadiene polymer	Cold polymerization	33	Bayer & Co., 1915-18	Germany.
Methyl rubber W	Dimethylbutadiene polymer	Hot polymerization	33	Bayer & Co., 1915-18	Germany.
Neoprene	Chloroprene polymer		60	E. I. du Pont de Nemours & Co.	United States.
Mustone	Chloroprene polymer		20	Umeno Institute	Japan.
Oppanol	Isobutene polymer		203	I. G. Farbenindustrie	Germany.
Perbunan	Butadiene copolymer	Copolymer with acrylonitrile.	128	I. G. Farbenindustrie	Germany.
Perbunan Extra	Butadiene copolymer	Copolymer with acrylonitrile—higher nitrile content than Perbunan.	128	I. G. Farbenindustrie	Germany.
Perduren	Organic polysulfide		183	I. G. Farbenindustrie	Germany.
Resinit*	Organic polysulfide		109	.....	Russia.
SKA	Butadiene polymer	From petroleum	116	.....	Russia.
SKB	Butadiene polymer	From alcohol	109	.....	Russia.
Sovprene	Chloroprene polymer		63	.....	Russia.
Thiokol	Organic polysulfide		180	Thiokol Corporation	United States.
Thionite	Organic polysulfide		172	.....	Japan.
Vistanex	Isobutene polymer		206	Standard Oil Co.	United States.
Vulcaplas	Organic polysulfide		176	Imperial Chemical Industries.	England.

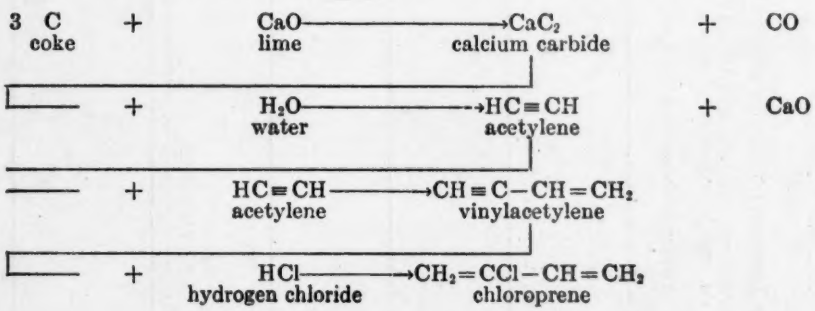
* This term is now commercially obsolete.

the materials shown in Tables I and II are at present in commercial production, although some are produced in very limited quantities. From the diversity of chemical constitutions shown by the examples in Table II, one may conclude that the physical properties ordinarily associated with rubber are not limited to one group of related chemical compounds, and that there are probably many more undiscovered types of synthetic rubber.

III. CHLOROPRENE POLYMERS

The preparation and properties of the chloroprene polymers have been described quite extensively in the scientific literature. Neoprene, formerly called Duprene, is the leading representative of this type, and is widely used in the United States and in England. The Russian chloroprene polymer is called Sovprene[63].

The chemical reactions[60, 71] involved in the manufacture of chloroprene are indicated by the following equations:



Chloroprene polymerizes much more rapidly than butadiene and, with a few unimportant exceptions, somewhat more rapidly than any of the derivatives of butadiene[73]. If the polymer is removed when polymerization is about one-third complete, it is found to possess quite different mechanical properties from those of the completely polymerized material[60]. The former product, the α-polymer, resembles unvulcanized rubber while the latter, the μ-polymer, resembles vulcanized rubber. The commercial varieties of Neoprene correspond to the α-polymer, and are made by the polymerization of chloroprene under different conditions. Neoprene G, for example, is an emulsion polymer[89]. A very small amount of a stabilizing material, commonly phenyl-β-naphthylamine, is usually added to Neoprene after polymerization[64, 93]. The stabilizer prevents continued polymerization, or more particularly cross-linking or cyclization, which would cause a stiffening of the Neoprene during storage. Plasticizers are frequently added in small amounts for the purpose of enabling the material to be processed more conveniently with the usual rubber machinery[83].

When Neoprene is heated, it undergoes a permanent change in physical properties similar to that involved in the vulcanization of rubber. The chloroprene polymers are unique among rubbers, synthetic or natural, in that this process can occur without the addition of other materials. In commercial practice, however, it is found more desirable to add a number of compounding ingredients. Several of the metallic oxides[83, 88], such as magnesium oxide, zinc

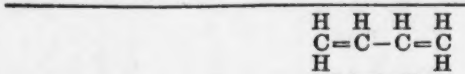
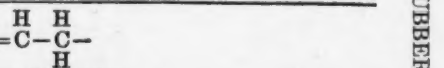
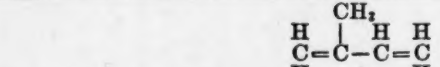
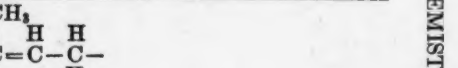
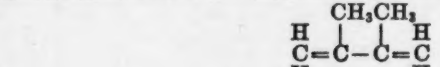
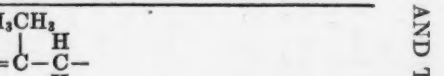
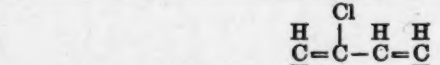
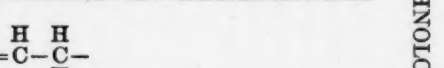
* This term is now commercially obsolete.

TABLE II

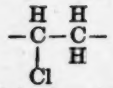
CHEMICAL STRUCTURES OF DIFFERENT VARIETIES OF SYNTHETIC RUBBER

NOTES.—The bonds between carbon and hydrogen are not indicated. The structural formulas are not intended to give any indications regarding stereoisomerism. Fuller[37] has recently suggested a ring structure in the organic polysulfides.

SIMPLE POLYMERS

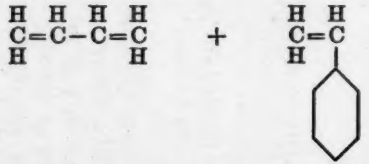
Monomer	Unit of polymer
 1,3-butadiene	 Buna 85, Buna 115, SKA, SKB, or Ker
 Isoprene (2-methyl-1,3-butadiene)	 Natural rubber
 2,3-dimethyl-1,3-butadiene	 Methyl rubber
 Chloroprene (2-chloro-1,3-butadiene)	 Neoprene, Sovprene, or Mustone
Isobutene (2-methyl-1-propene)	Vistanex, Oppanol

Vinyl chloride

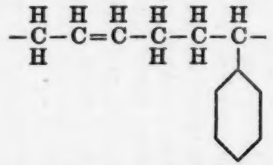


Plasticized materials:
Koroseal, Korogel, or Flamenol

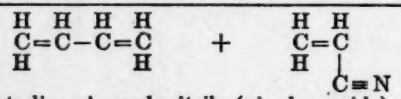
CO-POLYMERS



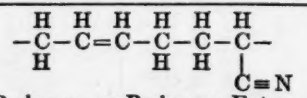
Butadiene+styrene (vinylbenzene)



Buna S or Buna SS

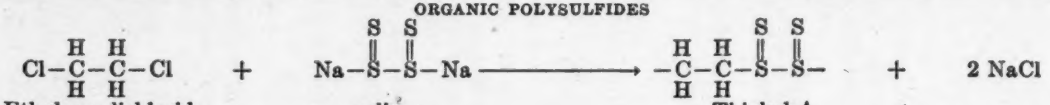


Butadiene+acrylonitrile (vinyl cyanide)



Perbunan or Perbunan Extra

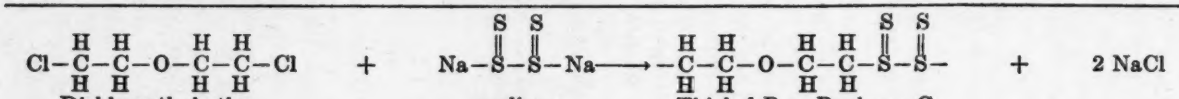
ORGANIC POLYSULFIDES



Ethylene dichloride
(1,2-dichloroethane)

sodium
tetrasulfide

Thiokol A



Dichloroethyl ether

sodium
tetrasulfide

Thiokol B or Perduren G

oxide, and litharge, function as vulcanizing agents, rather than sulfur, which when used, acts as an accelerator. Many of the organic accelerators used with natural rubber are not effective with Neoprene, but catechol and some similar substances are said to be promising substitutes[86, 90]. The addition of carbon black, which is usually found desirable, makes a stiffer compound, but, contrary to its effect with natural rubber, it does not increase the tensile strength. It has not been found possible to vulcanize Neoprene to a state corresponding to ebonite, or hard rubber. Compounding materials are mixed with Neoprene by means of the usual rubber machinery, but its behavior on milling is somewhat different. Neoprene E and the types previously produced appear to be unaffected by mastication, the softening which occurs being caused merely by the elevation of temperature. The newer types G, GW, and GN may be substantially softened by mastication[93].

IV. BUTADIENE POLYMERS

Butadiene, either alone or in combination with other substances, is the source of almost all the synthetic rubber manufactured in Europe. .Butadiene, a gas at temperatures above $-5°$ C, is being manufactured by a number of different methods. One method[133] involves the pyrolysis (cracking) of petroleum, especially the higher-boiling components. Under the proper conditions the process yields butadiene directly. The crude butadiene is then subjected to purification. This process is used in the manufacture of the Russian rubber called SKA[116], and it is reported to be the one which the Standard Oil Co. is planning to use in the United States for the manufacture of a rubber similar to Perbunan[112, 113, 117]. A dehydrogenation of some of the lower-boiling components of petroleum has also been described, but not yet put into commercial practice[134, 135].

In another important method, alcohol is converted into butadiene by a reaction[130] indicated by the following equation:

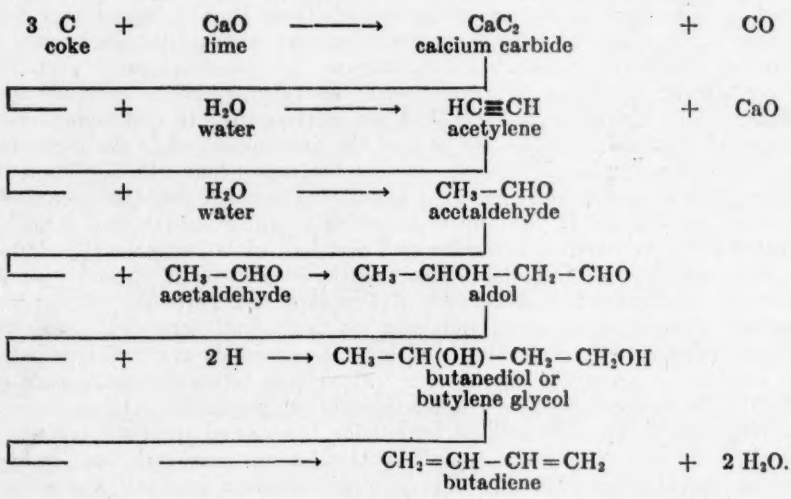
$$\underset{\text{alcohol}}{2C_2H_5OH} \rightarrow \underset{\text{butadiene}}{CH_2=CH-CH=CH_2} + 2H_2O + H_2.$$

The butadiene used in the manufacture of the Russian rubber SKB is prepared in this manner from alcohol obtained by the fermentation of grain or potatoes[109, 114, 131].

The polymerization of an impure material yields a product of low molecular weight, presumably because the formation of long chains is interrupted by the impurity. It is very difficult to obtain butadiene of high purity from petroleum products, especially when they are the products of cracking operations, or from agricultural products, particularly when they are obtained by fermentation. This fact is one of the major causes of difficulty and expense in the manufacture of butadiene from these sources.

One possible process for the manufacture of butadiene from acetylene is similar to that already given for the manufacture of chloroprene, except for the substitution of hydrogen for hydrogen chloride in the last step. However, the

reactions of the process[123, 140] actually used most extensively in Germany are indicated by the following equations:



Although long, the process is said to be free from side reactions, and to yield butadiene of high purity.

The first reaction is carried out in a furnace for which large amounts of electric energy are required[110]. The cost of the electric energy is probably one of the largest items in the whole process. In another process reported to be in use in Germany the acetylene is said to be extracted from coke-oven gases.

For the products known as Buna 85, Buna 115, SKA, and SKB, polymerization of butadiene is carried out with metallic sodium as the catalyst. Emulsion polymerization is used for Buna S and Perbunan. The copolymers Buna S and Perbunan contain 20 to 40 per cent of styrene[139] or acrylonitrile[138], respectively. Polymerization, in addition to the formation of the long chains, leads to a certain amount of cross-linking, or cyclization. The continuation of cyclization during storage of the raw material is prevented by the addition of a very small amount of a stabilizer, phenyl-β-naphthylamine being almost always used[128].

Buna S and Perbunan, in the uncompounded state, are somewhat stiffer than natural rubber, and they behave somewhat differently during processing on the usual rubber machinery. Heating Buna S to a temperature of 130° to 150° C for 1 or 2 hours in the presence of air produces a temporary change known as thermal oxidative softening, which is of very considerable importance in the technology of this material[142]. Since such a treatment is not effective with Perbunan, various softeners are usually added to facilitate processing.

Vulcanization of the butadiene polymers is carried out with sulfur as the vulcanizing agent, together with zinc oxide and organic accelerators. With sufficient sulfur, compounds of the ebonite type can be made[157]. In these respects the butadiene polymers are similar to natural rubber and differ from Neoprene. The ebonite made from the Buna rubber is said to soften at a higher temperature than that made from natural rubber[147].

V. ORGANIC POLYSULFIDES

The condensation reactions of organic dihalides with sodium tetrasulfide, indicated by the equations shown at the end of Table II, are typical of a large number of reactions[180, 183] for obtaining substances which, although bearing no chemical relation to natural rubber, conform to the definition of synthetic rubber already given. Certain products of this type are given the trade name Thiokol in the United States, and Perduren in Germany. In each unit of these compounds, two sulfur atoms are part of the main chain, while the two others are attached to them and are not part of the main chain. If the latter two sulfur atoms are removed by chemical means[180], Thiokol A yields an inextensible product, but Thiokol B yields material which is still extensible and is sold as Thiokol D[183]. Perduren G is similar to Thiokol B, while Perduren H is formed by the reaction of di(chloroethyl)formaldehydeacetal with sodium tetrasulfide[31, 183]. Perduren L is a mixture of Perduren and Perbunan. A Japanese product, Thionite, is obtained from the reaction of ethylene diglycoside with sodium tetrasulfide[172]. Vulcaplas is an organic polysulfide made in England by the reaction of glycerol dichlorohydrin with sodium tetrasulfide or similar sulfides[176]. The raw materials from which many of the polysulfide rubbers are made are relatively cheap. The sodium tetrasulfide is obtained from the reaction of caustic soda and sulfur; the organic dichlorides are produced from common organic compounds and chlorine. The chlorine is obtained from salt, and many of the organic compounds can be obtained from natural gas.

The polysulfide rubbers can be vulcanized, like Neoprene, with the metallic oxides as vulcanizing agents and sulfur as an accelerator. The chemical reaction must be of a type somewhat different from that in the vulcanization of natural rubber, where there is a decrease in the number of double bonds in the long-chain molecules; for the polysulfide rubbers, an oxidation with the evolution of water and an increase in chain length has been suggested[180]. Fillers are usually required for the development of satisfactory tensile strength. Carbon black is most frequently employed for this purpose.

The polysulfide rubbers, particularly Thiokol A, are by far the most resistant of the synthetic rubbers to the effects of liquids. Their chief disadvantages are a rather strong, unpleasant odor and some deficiency in mechanical properties. The odor has, however, been considerably reduced and rendered less objectionable in some of the newer varieties, and practically eliminated in others. Cold flow is a mechanical deficiency which can be reduced somewhat by increase of the amount of filler or by mixture with other types of rubber, natural or synthetic. Thiokol A is recommended for use only at temperatures between $-10°$ C and $+70°$ C, but many of the other types are serviceable from about $-40°$ C to $+80°$ C[190].

VI. ISOBUTENE POLYMERS

The polymerization of isobutene, a hydrocarbon obtainable from petroleum, gives a synthetic rubber which was developed in Germany under the name Oppanol[203]. Further research has continued in the United States, where the product is sold under the name Vistanex[206]. The polymerization is conducted at low temperatures with substances like boron fluoride or aluminum chloride as catalysts, and is extremely rapid, often being completed in a fraction of a second[200, 207]. The molecular weight of the product is controlled by the temperature at which polymerization occurs. For a temperature of $-10°$ C, the molecular weight, as measured by the Staudinger viscosity method, is about

10,000; for a temperature of −95° C, about 250,000. Isobutene polymers with molecular weights as high as 400,000 can be prepared in this manner[206].

Since the vulcanization of natural rubber is usually thought to be connected with a chemical reaction involving double bonds in the long-chain molecules, it is not surprising to note the failure of all attempts[206] to vulcanize isobutene polymers, which contain no double bonds.

Some writers[21, 128] prefer to use vulcanizability as one of the criteria for the classification of a material as a synthetic rubber. Consequently, contrary to the practice of the present paper, they do not include among synthetic rubbers the isobutene polymers, or the plasticized vinyl chloride polymers, discussed in the following section. Isobutene polymers maintain their elastic properties at temperatures as low as −50° C and as high as +100° C[32, 194, 204].

VII. PLASTICIZED VINYL CHLORIDE POLYMERS

Polymerized vinyl chloride is ordinarily obtained as an amorphous white powder, but by the application of pressure can be converted at 120° C into a transparent brittle solid, possessing a very small extensibility[219]. By itself it is not rubberlike; it has been found, however, that by the addition of a suitable liquid it may be plasticized to give an extensible material with an increase in the ultimate elongation up to about 500 per cent[212]. The amount of tricresyl phosphate, the plasticizer most commonly employed, may be as high as 60 per cent of the total. In the United States, Koroseal and Flamenol are the most widely used varieties of plasticized vinyl chloride polymers. The vinyl chloride polymers, like the isobutene polymers, contain no double bonds, as can be seen in Table II. Similarly, no method for their vulcanization has been discovered. No increase in tensile strength has been found when fillers are mixed with plasticized vinyl chloride polymers[212]. Since a reversible softening of the material occurs when it is heated, service temperatures above 77° C are not recommended[215].

Fuoss[219] has given an equation for the calculation of the specific volume, V, in cc. per g., of mixtures of polymerized vinyl chloride and tricresyl phosphate. His equation is equivalent to:

$$V = 0.706 + 0.155P,$$

where P is the weight of tricresyl phosphate expressed as a fraction of the total. A mixture of 40 per cent of tricresyl phosphate with polymerized vinyl chloride was found[217] to have a specific heat of 0.417 cal/g between 28° and 59° C and a thermal conductivity of $1.42 \pm 0.07 \times 10^{-3}$ j · sec^{-1} · cm^{-1} · deg^{-1} at temperatures between 50° and 100° C.

VIII. COMPARISON OF PROPERTIES

1. Densities

Values of the densities of a number of different varieties of synthetic rubber are shown in Table III. The temperature of the observation was seldom specified, but may be presumed to have been between 20° and 25° C. It will be noted, as might be expected, that the varieties consisting of hydrocarbons possess the lowest densities, while the varieties containing chlorine, namely Neoprene and Koroseal, and those containing sulfur, namely, the Thiokols and Perdurens, have higher densities.

TABLE III

DENSITIES OF UNVULCANIZED MATERIALS

Material	Density g. per cc.	Reference
Natural rubber	0.911	223
μ-Polymer of chloroprene	1.23	60
Neoprene	1.25	93
Perbunan	.96	128
Perbunan Extra	.97	128
Methyl rubber (20° C)	.9292	33
Thiokol A	1.60	190
Thiokol D	1.34	190
Thiokol DX	1.39	190
Thiokol F	1.38	190
Perduren G	1.68	31
Perduren H	1.56	31
Perduren L	1.17	31
Vistanex HM (25° C)	.9125	202
Vinyl chloride polymer containing 0% plasticizer	1.42	219
Vinyl chloride polymer containing 30% plasticizer	1.33	219
Vinyl chloride polymer containing 60% plasticizer	1.25	219

2. REFRACTIVE INDICES

The values of refractive index which have been reported are shown in Table IV.

TABLE IV

REFRACTIVE INDICES OF UNVULCANIZED MATERIALS

Material	Temperature, °C	n_D	Reference
Natural rubber	25	1.5190	227
μ-Polymer of chloroprene	20	1.5512	60
Neoprene	25	1.5580	51
Neoprene	30	1.5562	51
Perbunan	25	1.5213	51
Perbunan	30	1.5198	51
Methyl rubber	20	1.525	33
Vistanex HM	25	1.5089	209
Vistanex HM	10	1.5131	209
Components of plasticized vinyl chloride polymers:			
Vinyl chloride polymer (unplasticized)	40	1.565	219
Tricresyl phosphate (plasticized)	40	1.5494	219

3. IDENTITY PERIODS ALONG THE FIBER AXES

The x-ray patterns obtained when many of the varieties of synthetic rubber are stretched indicate the existence of a fiber structure during stress. Identity periods along the fiber axes have been reported, in Angstrom units, as follows:

Natural rubber	8.20 A[226]
μ-Polymer of chloroprene	4.81 A[60, 73, 75]
Thiokol A	4.32 or 8.64 A[37, 38]
Oppanol	18.50 A[196]
Vistanex	18.63 A[199]
Vinyl chloride polymer (unplasticized)	5.0 A[37]

4. Electrical Properties

The published data on the electrical properties of the various varieties of synthetic rubber are rather incomplete. The presence of polar groups—chlorine in Neoprene and Koroseal, and the nitrile group in Perbunan—is responsible for relatively high values of conductivity and dielectric constant in the types mentioned. The following values have been observed[102] at 28° C and are said to be representative of Neoprene compounds containing only enough added ingredients to insure proper vulcanization: dielectric constant at 1,000 c/s, 7.5; power factor at 1,000 c/s, 300×10^{-4}; and d-c conductivity, 10^{-12} mho · cm^{-1}. The electrical properties of Buna 85, Buna 115, and Buna S are nearly alike. Values reported[156] for a temperature of 20° C are dielectric constant at 50 c/s, 2.9; power factor at 50 c/s, 7×10^{-4}; and conductivity, $10^{-15}-10^{-14}$ mho · cm^{-1}. Perbunan, with its polar nitrile group, has a dielectric constant of the order of 15 and a conductivity of $10^{-7}-10^{-6}$ mho · cm^{-1} [158].

The same author[153] has more recently reported values for Buna S and Buna SS at 20° C as: dielectric constant at 50 c/s, 4.3 to 4.7; and power factor at 50 c/s, 170×10^{-4}. In the same work the conductivity of Perbunan was given as between 10^{-10} and 10^{-8} mho · cm^{-1}. The dielectric constant of a Thiokol compound has been reported as 4.60 [58]. Scott[205] has made some electrical measurements on Vistanex at 25° C. The dielectric constant at 1,000 c/s and at 100,000 c/s was found to be 2.29. The power factor at 1,000 c/s was measured at 1.5×10^{-4} and at 100,000 c/s as 3.4×10^{-4}. The d-c conductivity 1 minute after the application of the potential was less than 20×10^{-18} mho · cm^{-1}. The electrical properties of vinyl chloride polymers, plasticized with tricresyl phosphate, have been the subject of extensive studies by Fuoss[216, 217, 218, 219] and by Davies and Busse[213]. The results obtained are too detailed and complex for summary here, but a few values selected from one paper[219], reporting measurements at 40° C, are given below.

Plasticizer Per cent	Dielectric constant		Direct-current conductivity mho·cm^{-1}
	60 c/s	1,000 c/s	
0.....	3.435	3.338	0.1×10^{-12}
30.....	7.56	5.72	2.8×10^{-12}
60.....	10.18	9.65	$323.\times10^{-12}$

5. Tensile Strengths

The maximum reported values of the tensile strengths with the corresponding elongations for different kinds of synthetic rubber are given in Table V. Since the data were necessarily obtained from a number of sources, the conditions of measurement may not have been strictly comparable in all cases. In some instances, the figures have been rounded off from those actually observed. The figures refer, respectively, to the unvulcanized material, to a vulcanized compound containing no fillers, and to a vulcanized compound containing approximately the optimum amount of carbon black for maximum tensile strength in each case.

A study of Table V reveals a number of interesting facts. The major increase in tensile strength of natural rubber occurs on vulcanization; the effect of the addition of carbon black is to increase the tensile strength somewhat and to stiffen the rubber quite considerably. No synthetic rubber compounds have been made with tensile strengths exceeding those of the best carbon black compounds of natural rubber. Neoprene shows no increase in tensile strength with

TABLE V

MAXIMUM TENSILE STRENGTHS AND CORRESPONDING ELONGATIONS

Material	Unvulcanized			Vulcanized pure-gum compound			Vulcanized carbon-black compound		
	Tensile strength kg. per sq. cm.	Elongation %	Reference	Tensile strength kg. per sq. cm.	Elongation %	Reference	Tensile strength kg. per sq. cm.	Elongation %	Reference
Natural rubber	25	1,200	228	290	710	33	350	650	33
Neoprene	30	1,100	86	300	820	86	290	760	91
Buna 85	..	....	...	...	...	...	175	600	147
Buna 115	..	....	...	...	...	...	200	700	147
Buna S	..	....	...	...	...	...	280	650	147, 156
Perbunan	..	....	...	150	900	128	320	600	128
Methyl rubber W	..	....	...	30	510	33	170	530	33
Methyl rubber H	..	....	...	90	240	33	160	300	33
Thiokol A	..	....	...	...	...	...	60	370	183, 190
Thiokol D	7	570	179	35	750	190	120	610	179
Vistanex MM (Oppanol B100)	20	1,000	201						
Vistanex HM (Oppanol B200)	60	1,000	32, 201						
Koroseal 0% plasticizer	400	2	212	*	*	...	*	*	...
Koroseal 30% plasticizer	270	170	212						
Koroseal 60% plasticizer	70	500	212						

* Not vulcanizable.

the addition of carbon black, but undergoes a stiffening. Thiokol, very weak in the unvulcanized form, is markedly strengthened by vulcanization; by far the major increase in tensile strength, however, occurs on the addition of carbon black. Carbon black is also the major factor in obtaining high tensile strengths with Perbunan and the other types of Buna rubber, as well as with methyl rubber. Vistanex shows an increase of tensile strength with increasing molecular weight; the figures given are presumably for molecular weights of the order of 100,000 and 200,000, respectively. Koroseal is found to decrease in tensile strength and to increase in the corresponding elongation, as the amount of plasticizer is increased.

6. Superiorities of Synthetic Rubbers to Natural Rubber

The higher cost of synthetic rubbers is offset in a number of cases by the superiority of some of their properties in comparison with those of natural rubber. Foremost among these properties at present is resistance to the effects of liquids, particularly petroleum products. Table VI presents the results of swelling measurements for natural and synthetic rubbers in a number of liquids in which the swelling of natural rubber is particularly large. The figures have, in some cases, been rounded off from those actually observed. Since the data were necessarily obtained from a number of sources, the values, like those for tensile strength, may not be strictly comparable in all cases. However, the figures suffice to give an idea of the orders of magnitude involved and an idea of the relative swelling of different types of synthetic rubber.

Table VI

Swelling of Vulcanized Compounds in Liquids

[Volume increase, in per cent, after immersion for 8 weeks at room temperature]

Liquids	Natural rubber %	Neoprene %	Perbunan %	Perbunan Extra %	Thiokol A %	Thiokol D %	Thiokol DX, F %
Light gasoline (benzine)	160	...	20	20	0	...	...
Gasoline	230	8	40	...	0	3	3
Kerosine	...	60	...	...	0	2	2
Diesel oil	120	...	15	15	...	...	...
Fuel oil	...	...	...	...	0	10	10
Lubricating oil	...	40	—4	...	0	1	1
Paraffin oil	140	...	3	...	...	...	...
Transformer oil	150	...	5	...	...	...	...
Acetone	...	25	110	100	...	...	9
Benzene	370	160	210	140	7	150	90
Carbon tetrachloride	670	160	220	120	0	40	30
Ethyl ether	130	50	50	...	...	...	...
Linseed oil	100	...	20	...	...	1	1
Turpentine	300	90	50	30	0	...	...
References	156	96	31, 49, 156	31	190	190	190

The first eight liquids are petroleum products, in the handling of which synthetic rubber has been found particularly useful. Unfortunately, the common names used for the liquids are insufficient to describe their chemical compositions, which may vary widely with place of origin and subsequent treatment. Since the swelling is determined largely by the chemical composition of the liquid, such a wide variation of values is obtained that the figures quoted for these

products are less significant than those for the others. Neoprene, for example, may swell in different lubricating oils at 100° C as much as 120 per cent or as little as 12 per cent[95]. Correlation is found with a figure which represents to some extent the ratio of aliphatic to aromatic components in the oil.

For many uses, loss of tensile strength on swelling is an even more serious factor than actual swelling. Very little information on this subject has been published. Usually the tensile strength of a synthetic rubber shows less impairment than that of natural rubber, even when the amounts of swelling are not widely different. Synthetic compounds can be made which are greatly superior to natural rubber in that there is much less extraction of soluble material by liquids in contact with them.

The second important general superiority of many synthetic rubber compounds is their resistance to deterioration or aging under conditions which impair the utility of natural rubber. Some of these conditions are exposure to the oxygen of the atmosphere, to ozone from electric discharges, or to light, especially direct sunlight[102, 187] or to high temperatures[102, 147, 162]. Flex-cracking can also be considerably reduced or eliminated in many cases[91, 128].

Since the usual deterioration of natural rubber is thought to be connected with an oxidation reaction involving the double bonds, it is not surprising to note the superiority, in this regard, of isobutene polymers[206] and plasticized vinyl chloride polymers[212], which contain no double bonds.

Synthetic rubber compounds can be made which show a greatly decreased permeability to liquids and gases compared with natural rubber. Part of the advantage is due to the absence of proteins and other nonhydrocarbon components, and part to differences in structure. The diffusion constant for water is defined by Taylor, Herrmann, and Kemp[57] as the number of grams of water-vapor passing through 1 sq. cm. of the material 1 cm. thick in 1 hour under a differential pressure of 1 mm. of mercury. The values which they found are as follows:

Soft vulcanized rubber	6.66×10^{-8} g.·hr.$^{-1}$·cm·cm.$^{-2}$· (mm. of mercury)$^{-1}$.
Ebonite	1.51×10^{-8} g.·hr.$^{-1}$·cm·cm.$^{-2}$· (mm. of mercury)$^{-1}$.
Neoprene (vulcanized)	2.63×10^{-8} g.·hr.$^{-1}$·cm·cm.$^{-2}$· (mm. of mercury)$^{-1}$.
Thiokol A	0.22×10^{-8} g.·hr.$^{-1}$·cm·cm.$^{-2}$· (mm. of mercury)$^{-1}$.
Plasticized vinyl chloride polymer	3.85×10^{-8} g.·hr.$^{-1}$·cm·cm.$^{-2}$· (mm. of mercury)$^{-1}$.

Roelig[153] has given corresponding figures for the Buna rubbers. Buna SS has a lower permeability than natural rubber, especially when the unvulcanized materials are compared.

The permeability to gases, of several types of synthetic rubber, has been measured by Sager and Sucher[99], by Sager[189], and by Barrer[44]. "Permeability" is defined by the former observers as the number of cubic centimeters per minute passing through a membrane 1 cm. thick and 1 sq. cm. in cross-sectional area, when it separates air at atmospheric pressure from the gas at a pressure of 30 mm. of water above atmospheric. The mean values which they obtained for hydrogen at 25° C are as follows:

Rubber	24×10^{-6} cc.·min.$^{-1}$·cm.·cm.$^{-2}$.
Neoprene	4.2×10^{-6} cc.·min.$^{-1}$·cm.·cm.$^{-2}$.
Thiokol B	0.71×10^{-6} cc.·min.$^{-1}$·cm.·cm.$^{-2}$.
Thiokol D	1.5×10^{-6} cc.·min.$^{-1}$·cm.·cm.$^{-2}$.

Buna S, Buna 85, and Buna 115 possess about the same permeabilities to air as natural rubber does, but Perbunan vulcanizates show a permeability less than half as large[147, 153].

Since a very appreciable fraction of the weight of Neoprene and Koroseal consists of chlorine, these materials show a greater resistance to burning than natural rubber. They burn when a flame is applied, but combustion usually ceases when the flame is removed[91, 212].

Losses from abrasion measured in the laboratory are reported to be about the same for the best compounds of Buna 85 and Buna 115 as for a high-grade tire tread of natural rubber[147]. With Buna S, the abrasion is said to be about 25 per cent less and with Perbunan about 40 per cent less. The figures refer to a material containing no softener or plasticizer. With the addition of the plasticizers which are necessary for working the materials on ordinary rubber machinery, as is done in the manufacture of tires on a plant scale, the advantages in resistance to abrasion are considerably reduced. It is stated that road tests in which 40 test cars traveled about 750,000 miles showed losses from abrasion for tires of Buna S and Perbunan to be about 10 per cent less and about 30 per cent less, respectively, than for tires of natural rubber[161]. More recently the figure of 25 to 35 per cent has been given as the result of a long series of road tests on tires of Buna S[128]. The other varieties of synthetic rubber are either inferior to natural rubber in resistance to abrasion, or only slightly superior.

The absorption of energy by synthetic rubber during repeated stresses is generally greater than that for natural rubber[84, 102, 103, 104, 154, 160]. This quality, a disadvantage under many conditions, especially where it may lead to overheating of the rubber as in tires, is desirable in cases where the rapid damping of vibrations is important.

As has been already mentioned, emulsion polymerization yields a latex similar to that of natural rubber. The latices of Neoprene[60, 105a, 106] and Buna S[164] contain particles which are smaller than those in the latex of natural rubber and are more nearly uniform in size. Furthermore, they contain no organic impurities subject to putrefaction through bacterial action. Consequently, they are often used where the penetration of the latex into fine pores is of importance or where decomposition must be avoided. The latex of Thiokol A contains particles larger than those of natural rubber[193].

The electrical properties of some types of synthetic rubber, notably Vistanex[205] and Buna S[153, 156], may be superior to those of natural rubber. The presence of polar groups, as already mentioned, is responsible for relatively high values of conductivity in Neoprene, Perbunan, and Koroseal. This property may sometimes be turned to advantage as for example in the dissipation of undesired static charges.

IX. APPLICATIONS OF SYNTHETIC RUBBER

The applications of synthetic rubbers, like those of natural rubber, are so many and varied that it is impossible to do more than list some of the general fields and to illustrate with a few specific examples. In general there are possibilities for the use of synthetic rubber in every application of natural rubber, and in a number of additional fields from which natural rubber is barred by some of its deficiencies. No single type of synthetic rubber possesses outstanding advantages in all fields. However, for any given application it is usually possible to select a particular variety of synthetic rubber which excels natural rubber in some property of importance for that application. Possibly no individual synthetic rubber will ever have as wide a field of application as natural rubber, but collectively synthetic rubbers possess a marked advantage over natural rubber by reason of the diversity of properties which they afford.

The commercial applications of synthetic rubber throughout the world today are determined in part by considerations of national economy and in part by those of the inherent characteristics of the different varieties. More natural rubber is used in vehicle tires and tubes than in any other single field of application. Where considerations of national economy enter, notably in Germany and in Russia, synthetic rubber is used very extensively for this purpose. Elsewhere, however, its higher cost has thus far prevented anything more than experimental applications in this field, where the deficiencies of natural rubber are not particularly noticeable.

Buna S is at present the type of synthetic rubber in general use in Germany for tires, while Perbunan is generally reserved for those uses where resistance to the effects of liquids is important[128]. There are several important factors dictating the choice of Buna S rather than Perbunan for tires. It is cheaper to produce, and plasticization with hot air is possible. In adhesive properties Buna S is superior to Perbunan, although still inferior to natural rubber. Natural rubber, because of its greater adhesiveness and smaller energy absorption, is sometimes used for the carcass of a tire in which Buna S is used for the tread. A direct bonding between the two, without the use of intermediate material, is possible, but direct bonding is impossible between Perbunan and natural rubber. The lack of sufficient adhesiveness leads to difficulties in building tires with a large number of plies without the use of natural rubber. The manufacture of 4-ply and 6-ply passenger car tires exclusively from Buna S is said to be on a satisfactory basis, but some problems connected with the manufacture of heavy truck tires apparently have not yet been completely solved[111, 128].

Each of the properties in which synthetic rubbers may be superior to natural rubber, as mentioned in the preceding section, suggests possible applications for the former. Resistance to the effects of liquids, particularly hydrocarbons, is responsible for the very extensive use of synthetic rubber in hose and tubing, especially in the handling of petroleum products. In oil fields, refineries, tankers, filling stations, and in the automobile itself, petroleum products now usually pass through hose and tubing of synthetic rubber and into tanks which are sealed with it. Elsewhere in the automobile are many other parts which may come in contact with oil. More of them every year are being made of synthetic rubber or jacketed with it. The number of such parts at present on some cars is said to be as high as thirty or forty. For use in contact with oils, grease, fats, and many chemicals mountings for vibration absorption, conveyor belts, tires for industrial trucks, gaskets, and sealing devices are being made of synthetic rubber. Additional examples are shoe soles and heels, aprons, gloves, and similar articles for personal use under the same conditions. The relative stability of synthetic rubbers towards liquids is responsible for their increasing use in printers' rolls and blankets, engraving plates, and similar articles. Tubes for spraying equipment for paints and lacquers utilize synthetic rubber to advantage. Neoprene, Thiokol, and Koroseal are extensively used in these applications.

The electrical uses of synthetic rubber deserve special mention. As already noted, Vistanex, Buna S, and the numbered Bunas are the only varieties which show superiorities to natural rubber in respect to purely electrical properties. They are being used as insulation for wires and cables. For many uses, especially at low voltages, the other varieties, such as Neoprene, Thiokol, and Koroseal, may be used also for insulation. There is much wider application, however, of these other varieties as jackets over insulation of natural rubber. They are frequently used in this way to protect natural rubber from the effects of light, air, ozone, oils, and other deteriorating influences. In many types of cables, jackets of synthetic rubber are displacing the lead sheaths formerly used.

The properties of low permeability to gases and stability in direct sunlight have been responsible for the use of synthetic rubber in balloons, from small ones intended for meteorological observations to large passenger-carrying dirigibles. For example, the Goodyear airship *Resolute*, used for sightseeing flights, is covered with fabric coated with Neoprene.

The impregnation of silk, cotton, and other fabrics with synthetic rubber of better aging qualities than the natural opens a whole field of household and personal uses. A few examples of products of this type are umbrellas, raincoats, tablecloths, shower curtains, and garment bags. Koroseal, which can be obtained in an extremely wide variety of colors, is especially applicable in this field.

X. PRODUCTION FIGURES AND PRICES

The steady increase in production of each type of synthetic rubber has been accompanied in general by a decrease in price. Many types are still produced in such small quantities that an expanded scale of operations may yet bring drastic reductions in price. In Germany and Russia, the only foreign countries where significant amounts of synthetic rubber are being produced, political considerations enter into reports of production figures, and the controlled economy of these countries makes it almost impossible to compare costs with those elsewhere. Even when market prices are known, the foreign exchange situation of these countries renders impossible a really significant calculation for the conversion of currencies.

In Germany a plant at Schkopau with a capacity of 25,000 tons a year began production in April 1939[55]. Another at Huls, Westphalia, of the same capacity has been under construction, and is probably now in operation[3]. Recent Russian figures are not available, but estimates as high as 50,000 tons a year or more are not uncommon[115, 124].

Compared with these figures for the countries where synthetic rubber is used in tires, the production figures seem very small for the United States, where such is not the case. The total production of synthetic rubber of all types in the United States in 1939 probably did not exceed 2,500 tons. Frolich[8] has also recently made a similar estimate. Neoprene and Thiokol have been produced in far larger quantities than the other types.

The present market price of Neoprene is from 65 to 75 cents per pound, depending on the variety; that of Thiokol is from 35 to 60 cents per pound; that of Vistanex is from about 60 cents to a dollar per pound. Koroseal is not sold on the open market, but its price is estimated as being of the order of 50 or 60 cents per pound. The cost of the Buna rubbers has been stated to be less than four times the cost of the natural rubber[125]. Perbunan has been sold in the United States at about a dollar per pound, a figure in general agreement with this statement. The cost has probably been somewhat reduced by the recent very extensive expansion of production facilities already mentioned.

XI. BIBLIOGRAPHY

The bibliography cites with some degree of completeness the scientific literature of the decade 1930-1940, in which almost all the development of modern synthetic rubber has occurred. References to the patent literature are included only rarely. Brief summaries of almost 250 United States patents dealing with synthetic rubber have been given in a series of articles by Rossman[26]. The patents have also been discussed in some detail by Génin[10], Voge[32a], Whitby and Katz[33], and Midgley[18]. The Russian literature, which includes at least one

journal devoted exclusively to synthetic rubber, has not been exhaustively investigated, because the journals are not readily accessible, and most of the work has not had a great deal of influence outside of Russia. Sixteen references which have been found to be especially valuable or important are marked with an asterisk. Of the two books devoted exclusively to synthetic rubber the one by Schotz[28], published just before the beginning of the modern development of synthetic rubber, is chiefly of historical interest. The book by Naunton[19] includes much more recent information, and is particularly complete in its discussion of Neoprene.

REFERENCES

I. General Discussion, Covering Two or More Types

A. GENERAL SURVEY

[1] Anonymous, Federal Standard Stock Catalog, Sect. III, Part 7, Group ZZ, Div. bb, Synthetic rubber, March **1938** (Government Printing Office, Washington, D. C.)
[2] Barron, Present position of synthetic rubber, *Chem. Age* (London) **37**, 227 (1937).
[3] Blank, Synthetic rubberlike materials, *Automotive Ind.* **80**, 696 (1939).
[4] Bridgwater, Synthetic substances with rubberlike properties, *Mech. Eng.* **60**, 735 (1938); *Rubber Age* (N. Y.), **44**, 21 (1938).
[5] Cosler, Commercial applications of chloroprene and butadiene rubbers, *India Rubber World* **95**, No. 3, 43 (1936).
[6] Delorme, Rubber derivatives and synthetic elastic materials, *Rev. Gén. Mat. Plastiques* **15**, 35, 141 (1939).
[7] Fisher, Nomenclature of synthetic rubbers, *Ind. Eng. Chem.* **31**, 941 (1939).
[8] Frolich, Trends in the development of synthetic rubbers, *News Edition* (Am. Chem. Soc.) **18**, 285 (1940).
[9] Garner, The rubber industry's new raw materials, *India-Rubber J.* **94**, No. 18a, 23 (1937).
*[10] Génin, Synthetic rubbers and rubber substitutes, Chapter 6 in Book 2, Vol. 1, p. 399, in Bloc and Génin: "Encyclopédie Technologique du Caoutchouc" (Revue Générale du Caoutchouc, Paris, **1938**).
[11] Jacobs, The possibilities of synthetic rubbers in France, *Rev. Gén. Caoutchouc* **15**, 243 (1938).
[12] Jacobs, The terminology of synthetic rubbers, *Caoutchouc et Gutta-percha* **35**, 35 (1938).
[13] Kirchhof, Progress in the field of rubber and its synthetic substitutes, *Chem.-Ztg.* **60**, 721 and 745 (1936).
[14] Koningsberger, The synthesis of rubber, *Chem. Weekblad* **36**, 35 (1939).
*[15] Konrad, Synthetic rubber, Chapter 11, p. 437, in R. Houwink: "Chemie und Technologie der Kunststoffe" (Akademische Verlagsgesellschaft, Leipzig, **1939**)
[16] Lamel, Artificial rubber, *Oesterr. Chem.-Ztg.* **40**, 127 (1937).
[17] McPherson, Examination of materials claimed to be synthetic rubber, *India Rubber World* **101**, No. 4, 43 (1940).
[18] Midgley, Synthetic and substitute rubbers, Chapter 20, p. 677, in Davis and Blake, "Chemistry and Technology of Rubber" (Reinhold Publishing Corp., New York, N. Y., **1937**).
*[19] Naunton, "Synthetic Rubber" (Macmillan, London, **1937**).
[20] Naunton, Synthetic rubber, *Annual Report on Progress of Rubber Technology* **1**, 35 (1937); **2**, 31 (1938); **3**, 39 (1939).
[21] Patrick, Commercial synthetic rubber, *Modern Plastics* **14**, No. 2, 46 (1936).
[22] Patrick, Rubberlike resins, *Modern Plastics* **15**, No. 2, 36 (1937).
[23] Philpott, Artificial rubber, *Bull. Rubber Growers Assoc.*, **19**, 441 (1937).
[24] Pummerer, Scientific progress in the field of rubber 1929-33; Artificial rubber, *Angew. Chem.* **47**, 209 (1934).
[25] Pummerer, The history and importance of artificial rubber, "Technikgeschichte", Verein Deutsch. Ing. Verlag, Berlin, **1938**, p. 27.
[26] Rossman, Synthetic rubber, *India Rubber World* **94**, No. 2, 31 (1936) to **95**, No. 4, 54 (1937); 9 installments.
[27] Schatzel and Cassell, Synthetic elastic polymers in the cable industry, *Ind. Eng. Chem.* **31**, 945 (1939).
[28] Schotz, "Synthetic Rubber", E. Benn Ltd., London, **1926**.
[29] Semon, New elastic materials expanding the field for rubber, *Modern Plastics* **17**, No. 2, 67 (1939).
[30] Stevens, Synthetics and substitutes, *Bull. Rubber Growers Assoc.* **21**, 401 (1939).
*[31] Stöcklin, Development of swelling-resistant rubber-like materials in Germany, *Proc. Rubber Tech. Conference London* **1938**, p. 434; *India-Rubber J.* **98**, 344, 369 (1939).
[32] von Rosenberg, Plastics having rubberlike properties, *Proc. Rubber Tech. Conference London* **1938**, p. 450.
[32a] Voge, German patents relating to synthetic rubberlike materials, *India Rubber World* **102**, No. 1, 48 (1940); **102**, No. 2, 47 (1940).
*[33] Whitby and Katz, Synthetic rubber, *Ind. Eng. Chem.* **25**, 1204 and 1338 (1933); *Rubber Chem. Tech.* **7**, 40 (1934).

B. POLYMERIZATION AND STRUCTURE

[34] Carothers, Polymers and polyfunctionality, *Trans. Faraday Soc.* **32**, 39 (1936).
[35] Dostal and Mark, The mechanism of polymerization, *Trans. Faraday Soc.* **32**, 54 (1936).
[36] Dostal, Mark, and Raff, Mechanism of thermal polymerization and polycondensation, *Ind. Eng. Chem.* **29**, 595 (1937).
[37] Fuller, The investigation of synthetic linear polymers by x-rays, *Chem. Rev.* **26**, 143 (1940).

[38] Katz, X-ray spectrography of polymers and in particular those having a rubberlike extensibility, *Trans. Faraday Soc.* **32**, 77 (1936); *Rubber Chem. Tech.* **9**, 357 (1936).
[39] Wibaut, Chemical structure of natural rubber and of different varieties of artificial rubber, *India-Rubber J.* **92**, 609 (1936).

C. COMPOUNDING AND VULCANIZATION

[40] Anderson, Processing and applications of synthetic rubber, *Trans. Inst. Rubber Ind.* **14**, 266 (1939).
[41] Anonymous, Compounding of Neoprene and Thiokol and a tabular comparison of properties, *Vanderbilt News* **9**, No. 4, 55 (1939).

D. PROPERTIES

[42] Anonymous, Resistance of Duprene and Thiokol to Chemicals, *Chem. Met. Eng.* **39**, 318, 654 (1932).
[43] Anonymous, Rubber and like products, *Chem. Met. Eng.* **43**, 560 (1936); **45**, 660 (1938).
[44] Barrer, Permeation, diffusion, and solution of gases in organic polymers, *Trans. Faraday Soc.* **35**, 628 (1939).
[45] Busse, Structure and behavior of rubber in solvents, Chap. V, p. 181, in Davis and Blake: "Chemistry and Technology of Rubber", Reinhold Publishing Corp., New York, N. Y., **1937**.
[46] Carpenter and Twiss, Measuring the permeability of rubber to various gases, *Ind. Eng. Chem. Anal. Ed.* **12**, 99 (1940).
[47] Fleurent and Bary, Some characteristic properties of artificial rubbers, *Rev. Gén. Caoutchouc* **14**, No. 134, 3 (1937); *Bull. Soc. Chim.* **5**, 91 (1938).
[48] Garner and Robinson, Difficulties encountered in the preparation of synthetic rubbers resistant to oils, "Recueil des Communications à Congrès International de Paris", **1937**, p. 191, Revue Générale du Caoutchouc, Paris.
[49] Garner and Westhead, Some oil-aging properties of synthetic rubberlike materials, *Proc. Rubber Tech. Conference*, London, **1938**, p. 423.
[50] Habgood, Bonding [of natural rubber, synthetic rubbers, and metals], *Trans. Inst. Rubber Ind.* **13**, 136 (1937); *Rubber Chem. Tech.* **11**, 169 (1938).
[51] Jones, Refractometer studies on rubber-pigment mixtures, *Ind. Eng. Chem.* **32**, 331 (1940).
[52] Naunton, Jones, and Smith, Oil-resisting rubber, *Trans. Inst. Rubber Ind.* **9**, 169 (1933); *Rubber Chem. Tech.* **7**, 234 (1934).
[53] Okhrimenko, Influence of low temperatures on the stress-strain curves of mixtures containing Thiokol and Duprene, *J. Rubber Ind.* (U. S. S. R.) **12**, 321 (1935); *Chem. Abstracts* **29**, 7120 (1935).
[54] Rohde, Properties of oil-resistant synthetic rubbers, *Ind. Chim. Belge* **9**, 446 (1938).
[55] Saito, Experiments on synthetic and natural rubbers (in Japanese), *J. Soc. Rubber Ind. Japan* **10**, 15 (1937); *Chem. Abstracts* **31**, 6050 (1937).
[56] Sager, Rubber substitutes as coatings for balloon fabrics, *J. Aeronaut. Sciences* **3**, 63 (1935); *India Rubber World* **94**, No. 1. 31 (1936).
[57] Taylor, Herrmann, and Kemp, Diffusion of water through insulating materials, *Ind. Eng. Chem.* **28**, 1255 (1936).
[58] Wildschut, Electrical properties of technical rubber mixtures, *India-Rubber J.* **92**, No. 18a, 19 (1936).

II. Chloroprene Polymers

A. GENERAL SURVEY

[59] Bridgwater, Economics of synthetic rubber, *Ind. Eng. Chem.* **28**, 394 (1936).
[*60] Carothers, Williams, Collins, and Kirby, II A new synthetic rubber: chloroprene and its polymers, *J. Am. Chem. Soc.* **53**, 4203 (1931); *Rubber Chem. Tech.* **5**, 7 (1932).
[61] Cox, Neoprene: its properties and uses, *Soc. Chem. Ind. Victoria, Proc.* **38**, 19 (1938).
[62] Dumonthier, Neoprene G, *Rev. Gén. Caoutchouc* **16**, 101 (1939).
[63] Klebanskii, Tzyurikh, and Dolgopol'skii, Chloroprene synthetic rubber (Sovprene), *Bul. Acad. Sci. U. S. S. R.* No. 2, 189 (1935); *Rubber Chem. Tech.* **9**, 383 (1936).
[64] Proske, Neoprene, *Gummi-Ztg.* **53**, 393, 419, 443 (1939).

B. CHEMISTRY

[65] Carothers, Berchet, and Collins, The addition of hydrogen chloride to vinylacetylene, *J. Am. Chem. Soc.* **54**, 4066 (1932); *Rubber Chem. Tech.* **6**, 121 (1933).
[66] Carothers and Coffman, Homologs of chloroprene and their polymers, *J. Am. Chem. Soc.* **54**, 4071 (1932); *Rubber Chem. Tech.* **6**, 115 (1933).
[67] Jacobson and Carothers, 1-alkyl-2-chloro-1,3-butadienes and their polymers, *J. Am. Chem. Soc.* **55**, 1624 (1933).
[68] Carothers, Collins, and J. E. Kirby, The addition of hydrogen bromide to vinylacetylene, bromoprene, and dibromobutene, *J. Am. Chem. Soc.* **55**, 786 (1933).
[69] Hurukawa and Nakamura, Synthetic rubber from acetylene. Preparation of vinylacetylene. Synthesis of chloroprene. *J. Soc. Rubber Ind. Japan* **12**, 103 and 150 (1939); *Chem. Abstracts* **33**, 9717 (1939).
[70] Klebanskii and Rakhlina, Determination of the unsaturation of chloroprene polymers, *J. Gen. Chem.* (*U. S. S. R.*) **7**, 1299 (1937); *Chem. Abstracts* **31**, 6921 (1937).
[71] Nieuwland, Calcott, Downing, and Carter, I. Polymerization of acetylene, *J. Am. Chem. Soc.* **53**, 4197 (1931).

C. POLYMERIZATION AND STRUCTURE

[72] Bolland and Melville, Photochemical polymerization of chloroprene and related molecules, *Proc. Rubber Tech. Conference London* **1938**, p. 239.
[73] Carothers, The synthetic rubber problem, *Ind. Eng. Chem.* **26**, 30 (1934).
[74] Carothers, Kirby, and Collins, Polymerization of bromoprene, *J. Am. Chem. Soc.* **55**, 789 (1933); *Rubber Chem. Tech.* **6**, 317 (1933).

[75] Garbsch and von Susich, Roentgenographic examination of μ-polychloroprene, *Kautschuk* **8**, 122 (1932); *Rubber Chem. Tech.* **6**, 113 (1933).
[76] Klebanskii and Vasil'eva, The structure of synthetic types of rubber. Polychloroprenes, *J. prakt. Chem.* **144**, 251 (1936); *Rubber Chem. Tech.* **10**, 126 (1937).
[77] Kruilov, Investigation of the structure of rubber by means of electron diffraction, *J. Exp. and Theor. Phys. U. S. S. R.* **5**, 524 (1935); *Rubber Chem. Tech.* **9**, 409 (1936).
[78] Krylov, Electronographic analysis of chloroprene rubber, *Caoutchouc and Rubber (U. S. S. R.)* No. 2, 26 (1938); *Chem. Abstracts* **32**, 4825 (1938).
[79] Kubota, Polymerization of chloroprene as revealed by the Raman effect, *Bull. Chem. Soc. Japan* **13**, 678 (1938).
[80] Melville, Mechanism of polymerization reactions, *Trans. Inst. Rubber Ind.* **15**, 209 (1939).
[81] Williams and Walker, Effect of oxygen and water on polymerization of chloroprene, *Ind. Eng. Chem.* **25**, 199 (1933).
[82] Zhavoronkov and Ryumina-Alekhina, Polymerization of chloroprene in the presence of butadiene and other substances, *J. Rubber Ind. (U. S. S. R.)* No. 8, 912 (1936); *Chem. Abstracts* **31**, 3329 (1937).

D. COMPOUNDING AND VULCANIZATION

[83] Bridgwater and Krismann, Factors affecting the rate of vulcanization of chloroprene plastic polymers, *Ind. Eng. Chem.* **25**, 280 (1933); *Rubber Chem. Tech.* **6**, 309 (1933).
[84] Catton and Fraser, Effect of pigmentation on Neoprene G Compounds, *Ind. Eng. Chem.* **31**, 956 (1939).
[85] Clapson, Litharge as accelerator for chloroprene plastic polymers, *Ind. Eng. Chem.* **29**, 789 (1937).
[*86] Jones, The vulcanizing characteristics of Neoprene, *Proc. Rubber Tech. Conference London*, **1938**, p. 411.
[87] Starkweather and Walker, Softening agents in Neoprene, *India Rubber World* **97**, No. 3, 43 (1937).
[88] Starkweather and Walker, Influence of metallic oxides on Neoprene properties, *Ind. Eng. Chem.* **29**, 872 (1937).
[89] Starkweather and Youker, Plasticization of Neoprene G, *Ind. Eng. Chem.* **31**, 934 (1939).
[90] Torrence and Fraser, Effect of modifying agents on vulcanized Neoprene compounds *Ind. Eng. Chem.* **31**, 939 (1939).

E. PROPERTIES

[*91] Bridgwater, Physical properties of Duprene compounds, *Ind. Eng. Chem.* **26**, 33 (1934); *Rubber Chem. Tech.* **7**, 406 (1934); *India Rubber World* **90**, No. 1, 31 (1934).
[92] Bridgewater, Neoprene as a construction material for the chemical industry, *Trans. Am. Inst. Chem. Engrs.* **35**, 435 (1939).
[93] E. I. du Pont de Nemours, sales literature.
[94] Flosdorf and Webster, Relative permeabilities of Neoprene and rubber to air and moisture, *India Rubber World* **98**, No. 5, 33 (1938).
[95] Fraser, Effect of petroleum products on Neoprene vulcanizates. *Ind. Eng. Chem.* **32**, 320 (1940).
[*96] Hayden and Krismann, Effect of oils and chemicals on Duprene compounds, *Ind. Eng. Chem.* **25**, 1219 (1933); *Rubber Chem. Tech.* **7**, 393 (1934).
[97] Jacobs, Neoprene in mixtures resistant to oils and combustion, "Recueil des Communications à Congrès International de Paris", **1937**, p. 186.
[98] Kambara, The mechanism of the oil resistance of Neoprene, *J. Soc. Chem. Ind. Japan* **39**, supp. 319 (1936); *Rubber Chem Tech.* **10**, 312 (1937).
[99] Sager and Sucher, Permeability of Neoprene to gases, *J. Research Natl. Bur. Standards* **22**, 71 (1939); *Rubber Chem. Tech.* **12**, 875 (1939).
[100] Starkweather and Walker, Water resistance of Neoprene, *Ind. Eng. Chem.* **29**, 1380 (1937); *Rubber Chem. Tech.* **11**, 383 (1938).
[101] Yerzley, Adhesion of Neoprene to metal, *Ind. Eng. Chem.* **31**, 950 (1939); *Rubber Chem. Tech.* **13**, 950 (1939); *Rubber Chem. Tech.* **13**, 166 (1940).
[102] Yerzley, The evaluation of rubber and rubber-like compositions as vibration absorbers, *Ind. Eng. Chem., Anal. Ed.* **9**, 392 (1937); *Rubber Chem. Tech.* **10**, 827 (1937); *Rubber Age* (N. Y.) **2**, 179 (1937).
[103] Yerzley, Neoprene as a spring material, Am. Soc. Mechanical Engineers. Preprint **18** (Dec. 1939).
[104] Yerzley, A new oscillograph for routine tests of rubber and rubber-like materials, *Proc. Am. Soc. Testing Materials*, Preprint **96** (1939); *India Rubber World* **100**, No. 4, 43 (1939); *Rubber Chem. Tech.* **13**, 149 (1940).

F. SPECIAL APPLICATIONS

[105] Hayden, quoted in Duprene: its application in industry, *India-Rubber J.* **91**, 253 (1936).
[105a] Dales, Characteristics and utility of Neoprene latices, *India Rubber World* **102**, No. 1, 43 (1940).
[106] Flint, Neoprene latex, *Caoutchouc et Gutta-percha* **34**, 204 (1937).
[107] Starkweather and Wagner, Neoprene cements, *Ind. Eng. Chem.* **31**, 961 (1939); *India Rubber World* **100**, No. 6, 39 (1939); *Rubber Chem. Tech.* **13**, 159 (1940).

III. Butadiene Polymers

A. GENERAL SURVEY

[108] Akobianoff, Synthetic rubber and chemical products, *Rev. Gén. Caoutchouc* **11**, No. 103, 10 (1934); Development of the rubber industry in U. S. S. R., *Rev. Gén. Caoutchouc* **11**, No. 107, 24 (1934).
[109] Akobzhanov, Synthetic rubber. Its industrial production in the U. S. S. R., *Rev. Gén. Mat. Plastiques* **10**, 370 (1934); *Rubber Chem. Tech.* **8**, 430 (1935).
[110] Ambros, The new Buna plant, *Gummi-Ztg.* **53**, 561 (1939).
[111] Ambros, The synthetic rubber Buna, *Rev. Gén. Caoutchouc* **16**, 213 (1939).

[112] Anonymous, Buna, *The Lamp* (Standard Oil Co. of New Jersey), Feb. **1940**.
[113] Anonymous, Buna plant announced, *News Edition* (Am. Chem. Soc.) **18**, 300 (1940).
[114] Anonymous, Russian artificial rubber, *Chem.-Ztg.* **60**, 313 (1936).
[115] Anonymous, Russia's goal set at rubber independence, *Rubber Age* (N. Y.) **46**, 383 (1940).
[116] Buizov, Preparing rubber from petroleum, *J. App. Chem.* (*U. S. S. R.*) **6**, 1074 (1933); *Foreign Petroleum Tech.* **2**, 185 (1934); *Chem. Abstracts* **28**, 5711 (1934).
[117] Carmical, Synthetic rubber to be made here, *New York Times*, Feb. 11, 1940.
[118] Hagen, German artificial rubber, *Umschau* **43**, 488 (1939).
[119] Hofmann, Buna and war rubber from coal, *Naturwissenschaften* **24**, 428 (1936).
[120] Koch, Buna rubbers, *Ind. Eng. Chem.* **32**, 464 (1940).
[121] Konrad, The development of the synthesis of rubber in Germany [in German]. *Atti del X Congresso Internazionale di Chimica Roma*, **1938**, Vol. 4, p. 82.
[122] Konrad, History of the development of synthetic rubber in Germany, *Gummi-Ztg.* **50**, 13 (Jubilee number **1936**).
[123] Konrad, Synthetic rubber (Buna), *Kautschuk* **13**, 1 (1937).
[124] Ossipov-Schmidt, quoted in Synthetic rubber production in the U. S. S. R., *Chem. Ind.* **54**, 619 (1935).
[125] Phillips, Influence of the motorization of the army on the development of synthetic rubber in Germany, *Z. Ver. Deut. Ing.* **81**, 397 (1937).
[126] Smolenski, quoted in *India-Rubber J.* **92**, 772 (1936).
[127] Springer, Buna, the German substitute for rubber, *Osterr. Chem.-Ztg.* **42**, 215 (1939).
*[128] Stöcklin, Buna, *Trans. Inst. Rubber Ind.* **15**, 51 (1939).
[129] Stöcklin, Exchange of experiences in Buna manufacture, *Kautschuk* **15**, 117 (1939).

B. CHEMISTRY

[130] Lebedev, Preparation of bivinyl directly from alcohol, *J. Gen. Chem.* (*U. S. S. R.*) **3**, 698 (1933); *Chem. Abstracts* **28**, 3050 (1934).
[131] Nebovidsky, Manufacture of (Russian) synthetic rubber from ethyl alcohol, *Bull. Assoc. Chimistes* **55**, 215 (1938).
[132] Schultze and Schultze, Pyrolysis of ethylene, *Kautschuk* **15**, 182, 195 (1939).
[133] Tropsch, Thomas, Egloff, and Morrell, Olefins and conjugated dienes from gas oil, *Ind. Eng. Chem.* **30**, 169 (1938).
[134] von Grosse and Ipatieff, Catalytic dehydrogenation of gaseous paraffins, *Ind. Eng. Chem.* **32**, 268 (1940).
[135] von Grosse, Morrell, and Mavity, Catalytic dehydrogenation of monoolefins to diolefins, *Ind. Eng. Chem.* **32**, 309 (1940).

C. POLYMERIZATION

[136] Abkin and Medvedev, Kinetics of the polymerization of 1,3-butadiene in the presence of sodium, *Trans. Faraday Soc.* **32**, 286 (1936).
[137] Balandina, Berezan, Dobromyslova, Dogadkin, and Lapuk, Polymerization of butadiene in emulsions, *Bull. Acad. Sci. U. S. S. R.* p. 397, 409, and 423 (1936); *Chem. Abstracts* **31**, 4529 (1937).
[138] Konrad and Tschunkur (I. G. Farbenindustrie), U. S. Patent 1,973,000 (1934); German Patent 658,172 (1938).
[139] Tschunkur and Bock (I. G. Farbenindustrie), U. S. Patent 1,938,731 (1933); German Patent 570,980 (1933).
[140] Ziegler, Polymerization of butadiene and preparation of artificial rubber, *Chem.-Ztg.* **62**, 125 (1938); *Rubber Chem. Tech.* **11**, 501 (1938).

D. COMPOUNDING AND VULCANIZATION

[141] Capesius, The nerve of natural rubber and of Buna. *Gummi-Ztg.* **53**, 744 (1939).
*[142] Hagen, The plasticization of Buna (S), *Kautschuk* **14**, 203 (1938).
[143] Karmin, Some peculiarities of the vulcanization of synthetic rubber, *J. Rubber Ind.* (*U. S. S. R.*) No. 11, 1144 (1936); *Chem. Abstracts* **31**, 4531 (1937); **32**, 8832 (1938).

E. PROPERTIES

[144] Chesnokov, Dielectric properties of rubber mixtures prepared from synthetic rubber, *J. Rubber Ind.* (*U. S. S. R.*) No. 7, 792 (1936); No. 8, 921 (1936); *Chem. Abstracts* **31**, 8329 (1937).
[145] Gagina, Performance of automobile tires made of synthetic sodium-butadiene rubber, *Caoutchouc and Rubber* (*U. S. S. R.*) No. 12, 35 (1937); *Chem. Abstracts* **32**, 3197 (1938).
[146] Hagen, Comparative plasticity measurements of rubber and rubber mixtures with different plastometers, *Kautschuk* **15**, 88 (1939).
*[147] Koch, Specific properties of artificial (Buna) rubber, *Z. Ver Deut. Ing.* **80**, 963 (1936); *Rubber* Chem. Tech. **10**, 17 (1937).
[148] Lightbown, Some properties of Perbunan, *Rubber Age* (N. Y.) **47**, 19 (1940).
[149] Nowak and Hofmeier, Influence of rubber-like high polymers on physical properties of Buna mixtures, *Kautschuk* **14**, 193 (1938).
[150] Philippoff, Comparative viscosimetric investigations of solutions of crepe rubber and Buna, *Kautschuk* **13**, 149 (1937); *Rubber Chem. Tech.* **11**, 372 (1938).
[151] Philippoff, Determination of mechanical properties of natural and synthetic rubber, *Kautschuk*, **15**, 191 (1939).
[152] Roelig, Buna in cable application, *Elektro-Techn. Z.*, **59**, 172 (1938).
[153] Roelig, Buna in cable technique, *Kautschuk* **16**, 26 (1940).
[154] Roelig, Dynamic evaulation of the damping and fatigue resistance of vulcanizates, *Kautschuk* **15**, 7, 32 (1939).
[155] Roelig, New test methods for soft rubber, *Kautschuk* **13**, 154 (1937).
[156] Roelig, Technical applications of Buna in the chemical industry. I. Soft rubber from Buna, *Chem. Fabrik* **11**, 281 (1938).

[157] Roelig, Technical applications of Buna in the chemical industry. II. Hard rubber from Buna, *Chem. Fabrik* **12**, 481 (1939).
[158] Roelig, Technical properties of synthetic rubber, *Z. Ver. Deut. Ing.* **82**, 139 (1938); *Westdeutsche Techn. Blätter*, No. **12** (Dec. 1937).
[159] Roelig, Technical properties of synthetic rubber and new methods of measurement, *Kautschuk* **13**, 179 (1937).
[160] Rohde, Characterization of the plasto-elastic state, *Kautschuk* **15**, 64 (1939).
[161] Stadlinger, Synthetic rubber at the International Automobile and Motorcycle Exposition in Berlin 1936, *Chem.-Ztg.* **60**, 193 (1936).
[162] Stöcklin, Heat-resistant Buna mixtures, *Kautschuk* **15**, 1 (1939).

F. SPECIAL APPLICATIONS

[163] Andreev and Zingerevich, Influence of solvent on solution in reclaiming, *J. Rubber Ind.* (*U. S. S. R.*) **13**, 1174 (1936); *Chem. Abstracts* **31**, 6503 (1937).
[164] Bächle, The properties of Buna latex, *Kautschuk* **13**, 174 (1937).
[165] Badum, Use of Buna synthetic rubber as insulation for submarine cables, *Proc. Rubber Tech. Conference London*, **1938**, p. 463.
[166] F. W. H., Buna in the technical trade (Reclaim), *Gummi-Ztg.* **50**, 871 (1936).
[167] Kartzev and Verbo, Reclaiming of synthetic rubber by the solution method, *J. Rubber Ind.* (*U. S. S. R.*) **13**, 531 (1936); *Chem. Abstracts* **30**, 7384 (1936).
[168] Selivanova et al., Reclaiming of rubber from synthetic rubber, *Caoutchouc and Rubber* (*U. S. S. R.*) No. 11, 63 (1938); *Chem. Abstracts* **33**, 4457 (1939).
[169] Ziskind, Reclaiming of synthetic rubber by the method of swelling, *J. Rubber Ind.* (*U. S. S. R.*) **13**, 50 (1936); *Chem. Abstracts* **30**, 6603 (1936).

IV. Polysulfide Rubbers

A. GENERAL SURVEY

[170] Akobjanoff, Thiokol and mixtures resistant to organic solvents, *Caoutchouc et Gutta-percha* **33**, 17, 429, 17, 461 (1936).
[171] Anonymous, Ethanite, *India Rubber World* **89**, No. 6, 40 (1934).
[172] Anonymous, Japanese synthetic rubber, *India-Rubber J.* **92**, 760 (1936); **96**, 116 (1938).
[173] Borodulin, Economic prospects in using Thiokol in the rubber industry, *J. Rubber Ind.* (*U. S. S. R.*) **11**, 198 (1934); *Chem. Abstracts* **29**, 2779 (1935).
[174] Chernikov and Ostrerov, The use of Thiorubber in manufacturing, *J. Rubber Ind.* (*U. S. S. R.*) **11**, 228 (1934); *Chem. Abstracts* **29**, 2389 (1935).
[175] Harragan, Manufacture of Thiokol, *India Rubber World* **95**, No. 3, 38 (1936).
[176] Imperial Chemical Industries and R. F. Goldstein, British patent 453,850 (1935).
[177] Källner, Characteristics of Thiokol, *Kautschuk* **14**, 219 (1938).
[178] Kawano, Rubber-like substances derived from formalin, *J. Soc. Rubber Ind. Japan* **12**, 9 (1939); *Chem. Abstracts* **33**, 9717 (1939).
[179] Martin and Patrick, Constitution of polysulfide rubbers, *Ind. Eng. Chem.* **28**, 1144 (1936).
*[180] Patrick, Formation of high polymers by condensation between metallic polysulphides and dihalogenated hydrocarbons and ethers, *Trans. Faraday Soc.* **32**, 347 (1936); *Rubber Chem. Tech.* **9**, 373 (1936).
[181] Proske, Thiokol (A), *Angew. Chem.* **52**, 344 (1939).
[182] Smith, Thiokol, a solvent-resistant rubberlike material, *Kautschuk* **9**, 185 (1933).
*[183] Spielberger, Thioplasts, their preparation and application, *Kautschuk* **13**, 137 (1937).
[184] Spielberger, New oil-resistant rubberlike materials; Thioplasts, *Chem.-Ztg.* **63**, 29 (1939).

B. PROPERTIES

[185] Kartzev and Verbo, The resistance of Thiokol and its mixtures to benzene and oil, *J. Rubber Ind.* (*U. S. S. R.*) **11**, 319 (1934); *Chem. Abstracts* **29**, 8401 (1935).
[186] Kölbl, The processing of Thiokol, *Gummi-Ztg.* **53**, 1101, 1118, 1134 (1939).
[187] Martin, Sun-resistance of Thiokol-DX-rubber blends, *India Rubber World* **99**, No. 2, 38 (1938).
[188] Okhrimenko, Resistance to cold of raw Thiokol (Resinit), *J. Rubber Ind.* (*U. S. S. R.*) **12**, 75 (1935); *Chem. Abstracts* **29**, 6095 (1935).
[189] Sager, Permeability of organic polysulfide resins to hydrogen, *J. Research Natl. Bur. Standards* **19**, 181 (1937) RP1020; *Ind. Eng. Chem.* **29**, 747 (1937); *Rubber Chem. Tech.* **11**, 163 (1938); *India-Rubber J.* **94**, 512 (1937).
[190] Thiokol Corporation, sales literature.
[191] Zelinskii, Denisenko, Eventova, and Khromov, The source of Thiokol odor, *J. Rubber Ind.* (*U. S. S. R.*) **11**, 111 (1934); *Chem. Abstracts* **28**, 7590 (1934).

C. SPECIAL APPLICATIONS

[192] Anonymous, Thiokol as vulcanizing agent, *India Rubber World* **95**, No. 5, 38 (1937).
[193] Källner, Thiokol latex, *Chem. Fabrik* **12**, 418 (1939).

V. Isobutene Polymers

[194] Advance Solvents and Chemical Corp., sales literature.
[195] Anonymous, Vistanex a polymerized hydrocarbon, *Rubber Age* (N. Y.) **41**, 102 (1937).
[196] Brill and Halle, Rubber-like behavior of Oppanol when irradiated with X-rays, *Naturwissenschaften* **26**, 12 (1938); *Rubber Chem. Tech.* **11**, 687 (1938).
[197] Ferry and Parks, Glass formation by a hydrocarbon polymer, *J. Chem. Phys.* **4**, 70 (1936).
[198] Ferry and Parks, Viscous properties of polyisobutylene, *Physics* **6**, 356 (1935).

[199] Fuller, Frosch, and Pape, X-ray examination of polyisobutene, Paper presented at Cincinnati meeting of American Chemical Society, April **1940**. Abstract in *Rubber Age* (N. Y.) **46**, 375 (1940); *India Rubber World* **102**, No. 1, 61 (1940).
[200] Howard, U. S. Patent 2,049,062 (1936).
[201] I. G. Farbenindustrie, sales literature.
[202] McPherson, unpublished work.
[203] Schwarz, Oppanol B, a new polymeric hydrocarbon, *Kuntstoffe* **29**, 9 (1939).
[204] Schwarz, Synthetic materials, with special reference to the requirements of the rubber industry, *Kautschuk* **13**, 183 (1937).
[205] Scott, unpublished work.
*[206] Sparks, Lightbown, Turner, Frolich, and Klebsattel, Rubber-like properties of polybutene, *Ind. Eng. Chem.* **32**, 731 (1940).
[207] Thomas, Sparks, Frolich, Otto, and Mueller-Cunradi, Preparation and structure of high molecular weight polybutenes, *J. Am. Chem. Soc.* **62**, 276 (1940).
[208] Thomas, Zimmer, Turner, Rosen, and Frolich, Polybutenes. Properties and uses in petroleum products, *Ind. Eng. Chem.* **32**, 299 (1940).
[209] L. A. Wood, unpublished work.

VI. Plasticized Vinyl Chloride Polymers

[210] Anonymous, Korolac and Korogel, *Rubber Age* (N. Y.) **38**, 84 (1935).
[211] Brous, Koroseal, a raw material for the rubber industry, *India Rubber World* **101**, No. 3, 53 (1939).
*[212] Brous and Semon, Koroseal—a new plastic, *Ind. Eng. Chem.* **27**, 667 (1935); *Rubber Chem. Tech.* **8**, 641 (1935).
[213] Davies and Busse, Dielectric properties of plasticized polyvinyl chloride. Paper presented at Cincinnati meeting of American Chemical Society, April **1940**. Abstracts in *Rubber Age* (N. Y.) **46**, 375 (1940) and *India Rubber World* **102**, No. 1, 62 (1940).
[214] Fritz, Koroseal, *Product Eng.* **10**, 332 (1939).
[215] Fritz and Brous, Koroseal A. B. C.'s, *India Rubber World* **97**, No. 6, 41 (1938).
[216] Fuoss, Electrical properties of solids. II. Polyvinyl chloride-tricresyl phosphate, *J. Am. Chem. Soc.* **60**, 451 (1938).
[217] Fuoss, Electrical properties of solids. III. Thermal breakdown of plasticized polyvinyl chloride, *J. Am. Chem. Soc.* **60**, 456 (1938).
[218] Fuoss, Electrical properties of solids. IV. Influence of thermal history on polyvinyl chloride plastics, *J. Am. Chem. Soc.* **61**, 2329 (1939).
[219] Fuoss, Electrical properties of solids. V. Their variation at 40° C. with frequency and composition in the system polyvinyl chloride-tricresyl phosphate, *J. Am. Chem. Soc.* **61**, 2334 (1939).
[220] Russell, Behavior of polyvinyl chloride plastics under stress, *Ind. Eng. Chem.* **32**, 509 (1940).
[221] Schoenfeld, Koroseal as an engineering material, *Trans. Am. Inst. Chem. Engrs.* **35**, 447 (1939).
[222] Schoenfeld, Browne, and Brous, Recent developments with Koroseal, *Ind. Eng. Chem.* **31**, 964 (1939).

VII. Miscellaneous References

[223] Curtis, McPherson, and Scott, Density and electrical properties of the system, rubber-sulphur, Bur. Standards Sci. Paper No. **22**, 1927, p. 383, No. S560. Cf. Wood, Values of the physical constants of rubber, *Proc. Rubber Tech. Conference London*, **1938**, p. 933; *Rubber Chem. Tech.* **12**, 130 (1939).
[224] Dawson, On rubber terminology, *Proc. Rubber Tech. Conference London*, **1938**, p. 1003; *Rubber Chem. Tech.* **12**, 441 (1939).
[225] Houwink, The structure of the rubber macromolecule as related to the elastic properties of rubber, *India-Rubber J.* **92**, 457 (1936); Elasticity, plasticity, and the structure of matter, University Press, Cambridge, England, **1937**, p. 223.
[226] Lotmar and Meyer, The fine structure of crystallized rubber, *Montash.* **69**, 115 (1936); *Rubber Chem. Tech.* **10**, 242 (1937). Cf. Gehman, The contribution of x-ray research to the knowledge of rubber. *Chem. Rev.* **26**, 203 (1940).
[227] McPherson and Cummings, Refractive index of rubber, *J. Research Natl. Bur. Standards* **14**, 553 (1935); *Rubber Chem. Tech.* **8**, 421 (1935); Cf. L. A. Wood, Values of the physical constants of rubber, *Proc. Rubber Tech. Conference London*, **1938**, p. 933; *Rubber Chem. Tech.* **12**, 130 (1939).
[228] Rosbaud and Schmid, Stretching experiments on raw rubber, *Z. tech. Phys.* **9**, 98 (1928).

A STUDY OF POLYMERS *

I. HIGHLY ELASTIC DEFORMATION OF POLYMERS

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In the field of investigation of the phenomena of high elasticity the problems of most importance in the last few years have been:

1. The development of a kinetic theory of the nature of forces during highly elastic deformation[1-7], which would make possible a thermodynamic interpretation of the modulus of high elasticity;

2. The determination of the relaxation phenomenon of highly elastic deformation[8], making it possible to evaluate the kinetics of the process.

In the present work the temperature-time relation of the relaxation process of the highly elastic deformation of polymers is discussed.

It is regrettable that no generally accepted definition of "high elasticity" can be found in the literature. Measurements of highly elastic deformation[9] are not only purely conventional, but are incorrect, because they do not indicate the important difference between the mechanisms of ordinary elastic deformation and highly elastic deformation, which are not determinable by direct measurement. This is evident from the fact that the modulus of elasticity, when determined at various deformations of highly elastic materials, beginning with elongations of the order of 200-300 per cent and to deformations of the order of a few thousandths of one per cent (obtained in the determination of velocity of sound in rubbers[10, 11]), shows low values characteristic of highly elastic deformation, whereas high modulus values characteristic of substances which are not highly elastic are governed by factors other than the amplitude of deformation.

According to kinetic theories developed by Kuhn[2-4], Guth[5, 6], Mark[7], and other investigators, the basic difference between resilient and highly elastic deformation is that ordinary elastic deformation involves changes in the mean distances between the particles, whereas highly elastic deformation involves a rearrangement of the particles without any change in the mean distance between them. Let us examine at some length the nature of the two processes. In the absence of external forces, the mean distance between the particles of a substance is, in a general way, governed by the equality of the forces of attraction and repulsion. During elastic deformation, the external forces disturb this equality, and this results in a change in the distance between particles, the magnitude of which is such that the sum of all the forces acting on each particle becomes zero. As a result, there is an accumulation of elastic energy in the deformed sample. When the external force is removed, the entire system reverts to its original state, corresponding to a minimum of free energy. In this way the phenomenon of ordinary elasticity is fundamentally connected with changes in the distance between the particles. In highly elastic deformation, the situation is different. In the absence of external forces in highly elastic substances, as in all amorphous substances, a coördination in the arrangement of neighboring particles can exist at each moment, but without any macroscopic preferential orientation, *i.e.*, the mean distribution is unordered. The external forces cause a directed regrouping of the particles, which leads to (1) irreversible transposi-

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tions, *i.e.*, flow, and (2) transpositions, the result of which is a preferential orientation of particles in the system. This orientation in deformed highly elastic substances is confirmed by double refraction and by x-ray data[12, 15]. Thermal flow tends to disturb the orientation, which in itself is a cause of the force which counteracts the deforming force. On removing the external force, heat flow again brings the system into the original unoriented state. In this way, the original form of the sample is restored. The smaller is the effect of the irreversible rearrangements, the greater is this recovery. Proceeding from the supposition that the oriented and unoriented positions of particles are equivalent from an energy point of view, it follows that the density of a substance deformed in this way, as well as during flow, remains constant. Such a physical property of highly elastic deformation is in complete agreement with the kinetic theory; in fact it has been observed that during the highly elastic deformation of rubber[16], bakelite[17] and polyvinyl acetate[15], the volumes remain constant. Fillers and crystallization give cumulative effects, leading to changes in volume; these, however, can be computed. It is possible that in some substances the oriented and nonoriented distribution of particles may not be equivalent from an energy point of view. Such a possibility has been pointed out by Houwink[18]. In the further development of the theory of high elasticity, this point must be considered, although it is not considered in the present communication.

The reversible transposition of particles in a simple amorphous substance is limited by the size of the molecules, and therefore deformation accompanied with rearrangement is always accompanied also by a very considerable flow by plastic deformation. (The term "reversible" is used here and later, not in the thermodynamic sense, since such transpositions are always connected with a dispersion of energy, but in the sense of the spontaneous recovery of the original form on removal of the external forces.) In polymers, however, the reversible transposition of particles (separate links of the polymer chain) is limited by the length of the macromolecule, *i.e.*, it is considerably greater, while the irreversible deformation is made very difficult by the fact that the flow which occurs leads to a rearrangement of macromolecules as a whole. Hence, with increasing degree of polymerization, and particularly in the formation of spatial polymers, the function of irreversible deformation becomes less important, and basically deformation comprises the deformation which involves the reversible, oriented rearrangement of particles.

The following discussion deals with reversible deformation, and flow will not be considered. When an external force acts on a substance, it undergoes deformation of two types, ordinary elastic and highly elastic deformations, the actual deformation being their sum. Each deformation is governed by the corresponding modulus. For the deformation equivalent to the applied force (*i.e.*, not changing with time):

$$D = D_{el\infty} + D_{res} = \frac{1}{E_{el\infty}} + \frac{1}{E_{res}} = \frac{1}{E}, \qquad (1)$$

where D, $D_{el\infty}$ and D_{res}, the reciprocals of the corresponding moduli, are proportional to the relative deformations (for a given tension). E_{res} is the modulus of Jung, and represents the elastic part of the deformation; $E_{el\infty}$ is the modulus of highly elastic deformation; E is the complete modulus. In this case, $D_{el\infty}$ is a function of the mean degree of orientation, and is represented by the static equilibrium between the external field and the unoriented action of the heat flow. The external field can be considered as the sole factor which influences orientation until a point is reached where the changes of reciprocal energy of

particles can be disregarded. For short experimental periods at low temperatures[8], in which case the oriented rearrangement of the particles proceeds very slowly, it is found that $D_{res}=1/E_{res}$, with E_{res} reaching 40,000 kg. per sq. cm. In measurements of the modulus of natural rubber at room temperature, the values are of the order of 20 kg. per sq. cm., *i.e.*, 2000 times lower. It follows that at room temperatures the deformation of rubber is related fundamentally to the process of regrouping of particles, and proceeds without change of volume. At lower moduli, when ordinary elastic deformation constitutes a substantial part of the actual deformation of a sample, the change in volume should be considerably greater. The observed deformation of an elastic substance can be represented schematically as consisting of two components which differ in their mechanisms. Ordinary elastic deformation follows the general rules observed by various investigators with metals and other materials. Elastic deformation, independent of the temperature, changes with a change in force, and its modulus depends but little on the temperature (corresponding to a comparatively small change of density with temperature).

Highly elastic deformation is connected with a regrouping of the particles and, therefore, in time it falls behind the change of force and is shifted in phase by a certain angle, depending on the mobility of particles. This shift in phase is related to the internal friction caused by interaction of neighboring particles, a fact which is not taken into account by the kinetic theory. The equilibrium values of highly elastic deformation can be calculated from known models, as was shown by Kuhn, Guth, Mark and other investigators. According to their data, $D_{el\infty}$ depends on the temperature, and thus affects the mean degree of orientation. This dependence, according to Mark, is:

$$E_{el\infty}=\frac{1}{D_{el\infty}}=\frac{7RT}{M}\rho, \tag{2}$$

where R is the gas constant, M is the molecular weight, ρ is density and T the absolute temperature. However, this dependence is not very great, and the influence of temperature on the deformation of rubbers usually observed is related fundamentally to the kinetics of highly elastic deformation. The probability of transition under the action of unordered heat flow of particles from position A to position A', which is effected only by surmounting the potential barrier U, is equal to:

$$W=Ce^{\frac{U}{kT}}, \tag{3}$$

where C is a coefficient, k is the Bolzmann constant and T is absolute temperature.

The value U of the potential barrier depends on the chemical nature and density of the substance and to some extent on the temperature. In the establishment of deforming forces, the process of regrouping becomes directed, and leads to a decrease in tension originating in the substance. The process of relaxation of tension in a deformed substance, observed by Maxwell, represents a classic example of macroscopic adjustment of a material to an external force as a result of irreversible regrouping of particles. In the future, all processes whose temporary course is governed by the probability of regrouping of particles under the action of heat flow will be grouped under the general term of relaxation processes.

In this, the relaxation processes related to irreversible regrouping lower the tension to zero (at a given deformation), or lead to flow at a constant velocity (under a given force); the relaxation processes connected with the increase in

preferential orientation lower the tension to a final value, or lead to a change of form approximately its equivalent. The velocity of highly varied relaxation processes is proportional to the probability of regrouping of particles W, *i.e.*, to the value $e^{-\frac{U}{kT}}$. With increasing temperature this velocity rises rapidly.

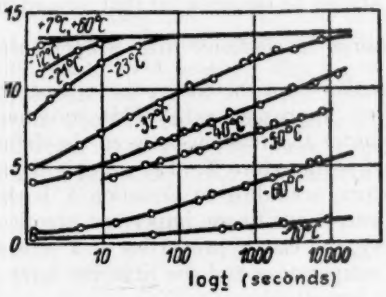

FIG. 1.—The relation between the deformation of rubber and the time of action of a force at different temperatures (according to Kobenko, Kuvshinskiĭ and Gurevich).

These data for the phenomena of highly elastic deformation were obtained by Kobeko, Kuvshinskiĭ and Gurevich[8], who showed that the integral elastic deformation of rubber does not depend to any great extent on the temperature (Figure 1). This proves that the deformation of highly elastic substances represents a reversible relaxation process.

As was shown above, the complete deformation of a sample equivalent to a given force can be expressed by the equation:

$$D=D_{el\infty}+D_{res}$$

To describe the course of the process of elastic deformation, it is necessary to introduce into the equation the value D_{elt} in place of the final, equivalent value $D_{el\infty}$. Its dependence on time $D_{elt}=f(t)$, obtained experimentally, is highly complex, and depends in part on the history of the sample. Hence the mathematical interpretation of elastic deformation can be effected by the application of functionals. This procedure, however, involves the use of highly complicated conventional apparatus, and does not aid in the elucidation of the physical picture of the processes involved. As a means to a clearer description of the physical nature of the process, it was found helpful to make a very rough approximation by assuming that the relaxation process in the determination of highly elastic deformation by the action of a constant force follows the exponential law. In this case the equation is:

$$D_{elt}=D_{el\infty}\left(1-e^{-\frac{t}{\tau}}\right),$$

where t is the time from the moment of application of force to the moment of reading the deformation; τ is the time of relaxation of the elastic substance, depending on the probability of regrouping the particles:

$$\tau=\frac{A}{e^{-\frac{U}{kT}}}=Ae^{\frac{U}{kT}} \qquad (4)$$

The complete deformation is then expressed by the equation:

$$D(t,T)=D_{el}+D_{el\infty}\left(1-e^{-\frac{t}{\tau}}\right)=D_{res}+D_{el\infty}\left(1-e^{Ae^{-\frac{t}{\frac{U}{kT}}}}\right) \quad (5)$$

(In this connection it should be remembered that, according to the kinetic theory, $D_{el\infty}\sim\frac{1}{T}$, but the change in elasticity with temperature, related to this function, is many times smaller than the one in the exponent; hence, it is not taken into account in a first approximation.) This equation will be used in the schematic interpretation of the relation between the deformation of elastic substances and time t and temperature T. The graphic dependence of deformation on time and temperature, according to Equation 5, is shown in Figure 2. The nature of this dependence leads to the important practical deduction that, even in an approximate way, the elastic properties of a substance must contain two parameters, *viz.*, the temperature and the time the force acts (or the frequency in the case of periodic forces).

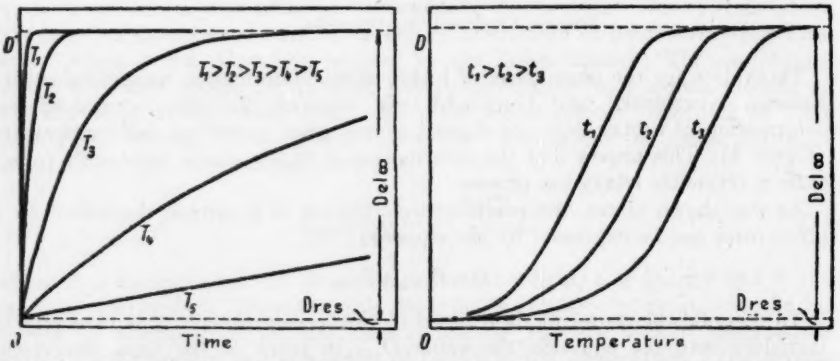

FIG. 2.—The dependence of deformation on the time of action of a force at different temperatures (left-hand graph) and on the temperature at different periods of time of the action of a force (right-hand graph), according to Equation 5.

Thus by proceeding from the definition of the deformation of elastic substances as a sum of the components of ordinary elastic and highly elastic relaxation, it is possible to obtain a schematic law representing the relation between elastic forces and the time of action of these forces and the temperature. Similar curves of the deformation by torsion were obtained by Kobeko, Kuvshinshiĭ and Gurevich. The usual measurements of the relation between deformation by stretching and temperature are also represented qualitatively by this relation. A thorough investigation of the time and temperature relations of highly elastic deformation was carried out with periodic forces. To this end, a laboratory apparatus was constructed, with the aid of which elasticity was studied within a range of temperatures of −180° C to 200° C. In this apparatus, a sample was subjected to periodic deformation by compression, in such a way that the deforming force changed with time sinusoidally. The frequency of the changing force varied within the limits of 1 to 1000 vibrations per minute, while the amplitude remained constant. (The apparatus and the method of measurement are described in Part II by Yu. S. Lazurkin). If a specimen is

subjected to a periodic force, then instead of Equation 5, which expresses the relation between deformation and time and temperature, we obtain for the amplitude of forced vibrations:

$$D=D_{res}+\frac{D_{el\infty}}{1+i\omega\tau}, \tag{6}$$

where i is $\sqrt{-1}$, ω is the frequency, and τ is the time of relaxation. Equation 6 appears to be complex, because, as previously noted, the relaxation deformation lags in phase behind the applied tension. This lag in phase is expressed in elastic substances by hysteresis and evolution of heat, *i.e.*, mechanical losses during deformation, known as the irreversible Joule effect. The relations between deformation and mechanical losses can be more conveniently denoted by separating deformation D in Equation 6 into its qualitative D' and apparent D'' components:

$$D=D'-iD'',$$

where

$$D'=D_{res}+\frac{D_{el\infty}}{1+\omega^2\tau^2} \tag{7}$$

and

$$D''=\frac{D_{el\infty}\omega\tau}{1+\omega^2\tau^2}. \tag{8}$$

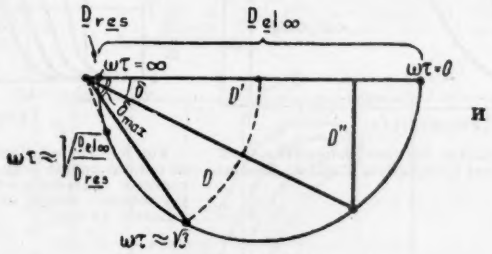

FIG. 3.

To show the deformation visually, the vector diagram is shown in Figure 3. Kuvshinskĭ used this type of diagram in describing analogous processes of dielectric polarization and losses. In this diagram the segment D_{el} denotes elastic deformation and $D_{el\infty}$ complete elastic deformation. The observed deformation is shown by segment D. Each point on the periphery corresponds to a definite value of the product $\omega\tau$. At $\omega\tau \to 0$ (low frequency or high temperature)

$$D=D_{el\infty}+D_{res}$$

At $\omega\tau \to \infty$ (high frequency or low temperature) $D=D_{res}$. In the intermediate values of $\omega\tau$, the observed deformation is complex, but its absolute magnitude can be calculated by the equation:

$$|D|=\sqrt{D'^2+D''^2}.$$

The angle δ indicates the shift of phases between the tension vector coinciding in direction with vectors D_{res} and $D_{el\infty}$, and vector D. Equations 7 and 8 make it possible to determine clearly the relation between $|D|$ and the temperature and frequency. The relation between $|D|$ and the temperature at various frequencies is shown in Figure 4. Figure 5 shows measurements of the deformation

of natural rubber, with 3 per cent sulfur, subjected to a periodic force. (In this and the following graphs, the doubled amplitude of deformation is projected on the ordinate axis. The doubled amplitude of force was equal to 2.7 kg. Measurements of cylindrical specimens are given at the bottom of the corresponding graphs). The graphs show that the central character of the relation conforms to the scheme described. From Figure 5 it can be seen that a substance, elastic at vibrations of low frequency, becomes as hard as glass at vibrations of higher frequency at the same temperatures. With higher values of ω highly elastic deformation has no time to develop, and the deformation is governed substantially by the ordinary elastic component. The same is obtained with higher τ values, *i.e.*, at lower temperatures. This ordinary elastic deformation is lower than the highly elastic deformation by, say, 2000 times, and cannot be shown

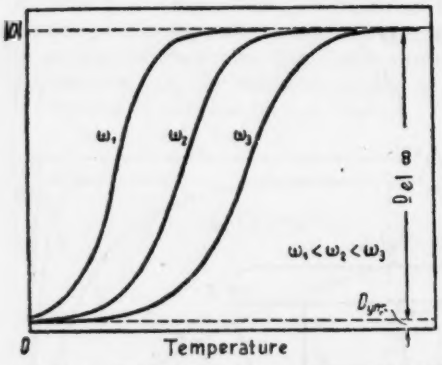

FIG. 4.—The relation between deformation and temperature, obtained by equations 7 and 8. Parameter—frequency.

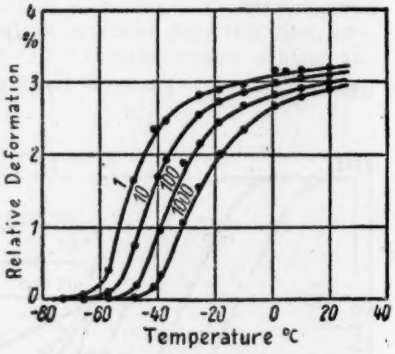

FIG. 5.—The relation between the deformation of natural rubber with 3% sulfur and the temperature. Parameter—frequency and vibrations per minute. Height of specimens 2.4 mm. and diameter 12 mm.

in our graphs. Therefore, with decreasing temperature the curves become closer to the axis of abscissas.

With low τ values or at low frequencies, as follows from the foregoing, the deformation is governed by $D_{el\infty}$. Figures 6, 7 and 8 give the results of analogous measurements of other polymers, *viz.*, chloroprene polymerized at room temperature and then heated 4 hours more at 145° C (Figure 6); methylmethacrylate resin with various percentages of plasticizer (Figure 7), and semivulcanized ebonite (Figure 8). In the case of ebonite, vulcanization continues at elevated temperatures, and this leads to decreased deformation. In all cases, the same general relation holds true. Dependence on the frequency, as evident in the upper part of the curves, and the corresponding losses (cf., *e.g.*, Figure 10, the losses in rubber) is not predictable by our scheme and is related to the difference between the real form of the curve and the exponent. Methylmethacrylate resin, hard at room temperature, behaves at higher temperature quite like rubber. Their complete moduli are closely related in magnitude. Styrene polymers behave similarly. Introduction of a plasticizer decreases the complete modulus and increases the speed of deformation at a given temperature. Combined sulfur in rubber tends to increase the modulus and the time of relaxation, *i.e.*, shifts the curves to higher temperatures. The polymers under investigation differ considerably in their structure and properties. Among them are spatial polymers with different numbers of transverse bonds and linear polymers,

with and without plasticizers. It follows that in most cases the dependence of the deformation of highly elastic substances on temperature and frequency is governed by the relation between the time of relaxation and the time during which the force acts, *i.e.*, it does not show any structure changes. In all cases, there is no definite temperature, or even temperature intervals, of transition from the elastic to the rigid state, and the entire range of cases observed showed

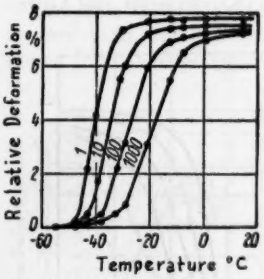

FIG. 6.—The same as in Figure 5 but for chloroprene polymer. Height of specimen 5.5 mm.; diameter 12 mm.

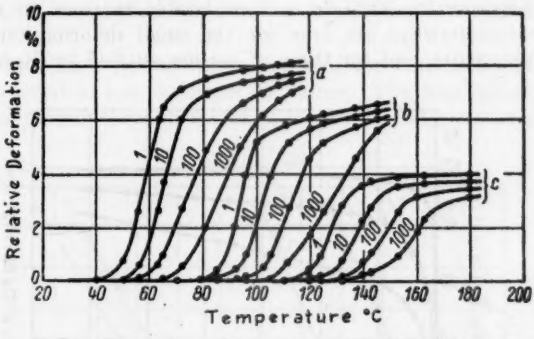

FIG. 7.—The same as in Figure 5, but for methyl methacrylate polymer: (a) with 30% plasticizer; (b) with 10% plasticizer; (c) without the plasticizer. Height of specimen 4.5 mm.; diameter 13 mm.

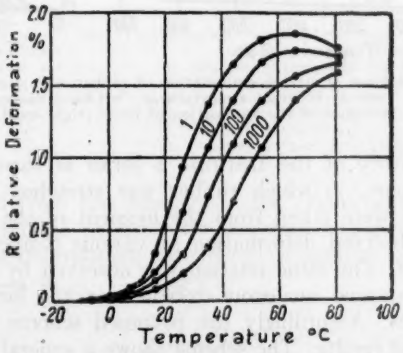

FIG. 8.—The same as in Figure 5, but for semivulcanized ebonite. Height of specimen 4.6 mm.; diameter 12 mm.

that the transition temperature is a function, not only of the nature of the substance, but also of the method of measurement (frequency or time of action). This is a general rule for all amorphous substances, and it must be taken into account in the production of articles from plastic and elastic materials. This observation applies in particular to the great number of rubber articles which are subjected to dynamic forces in service, *e.g.*, automobile tires, conveyor and transmission belts, shock absorbing devices, etc.

An increase in the frequency of the applied force has the same effect as a decrease in temperature. Within certain limits an increase in frequency influences comparatively little the behavior of an elastic substance, as has been shown by several investigators[20-25]. However, when $1/\omega$ and τ become nearly

the same, the behavior of a substance differs sharply. For example, at room temperature a change in frequency from 1 to 1000 vibrations per minute results in a 10 per cent change in the modulus of natural, unloaded rubber, whereas at −40° C under similar conditions the modulus is changed 10-fold (Figure 5). Obviously the use of rubber within these temperatures and frequencies is very limited. In the case of rubbers containing considerable sulfur or containing fillers which decrease the velocity of relaxation, the increase in frequency even at room temperature leads to a considerable increase in modulus[19, 28]. The foregoing characteristics are true for the small deformations of compression in our experiments, and for those of torsion studied by Kobenko, Kuvshinskiĭ and Gurevich[8]. In the laboratory of the Institute a series of experiments was carried out by P. G. Stepanov, in which rubber was stretched to 100 per cent of elongation. Readings were taken from the moment of the application of force to the moment of observed deformation at various temperatures. The results are given in Figure 9. The same relation was observed by Morey for synthetic rubbers. Hetenyi[17] showed analogous relations in the bending of bakelite at elevated temperatures. Accordingly the proposed scheme is in full agreement with the experimental results. The scheme shows a general relation for the mechanical losses in deformation of highly elastic substances. In the foregoing the angle of phase shift between the force and deformation was designated by δ. This angle can be measured directly, and its magnitude can be expressed, with the aid of Equations 7 and 8, by the relation:

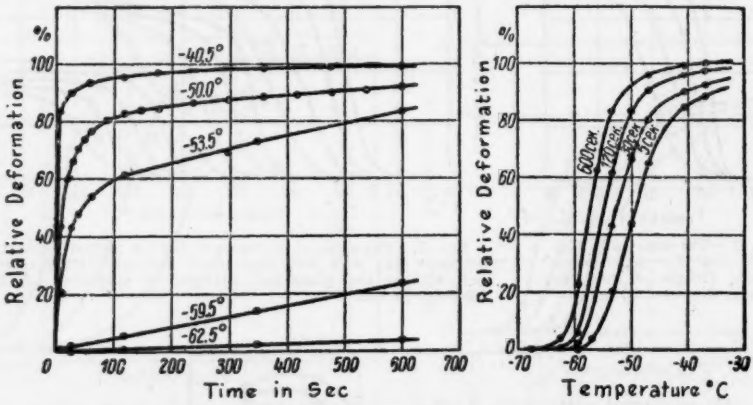

FIG. 9.—The dependence of stretch deformation of rubber with 3 per cent sulfur on the time of the applied force at different temperatures (left-hand diagram) and on the temperature at different durations of the application of force (right-hand diagram).

$$\tan\delta = \frac{D''}{D'} = \frac{D_{el\infty}\omega\tau}{D_{res}(1+\omega^2\tau^2)+D_{el\infty}} \tag{9}$$

This magnitude passes through its maximum at

$$\omega\tau = \sqrt{\frac{D_{el\infty}}{D_{res}}+1} \tag{10}$$

In the vector diagram (Figure 3) the maximum loss angle corresponds to the point when the vector D is tangent to the periphery (the vector is indicated

by dots). The diagram shows that under these conditions the observed deformation constitutes only a small part of the complete deformation, and the loss angle is approximately 90° (because D_{el} for rubber is small in comparison with $D_{el\infty}$). In fact the maximum of angle of mechanical losses in rubber was observed for the first time by E. V. Kuvshinskiĭ (work not published). The maximum mechanical losses of rubber and ebonite were determined by Mikhaĭlov and Kirilina[22] and Kornfel'd and Poznyak[23]. By means of a Kornfel'd vibrator, the present authors measured the mechanical losses of natural rubber containing 3 per cent of sulfur.

The graphs in Figure 10 show that the maximum angle of mechanical losses is very high, and that it is reached at low deformation values. The mechanical losses for other polymers also passed through maxima at definite temperature,

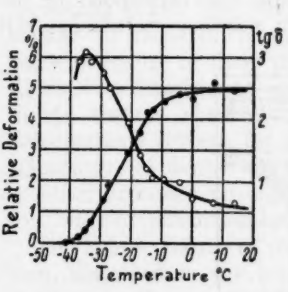

FIG. 10.—Deformation of rubber containing 3% sulfur and the angle of mechanical losses at a frequency of 2000 vibrations per minute.
. . . . . Deformation
o o o o o Losses

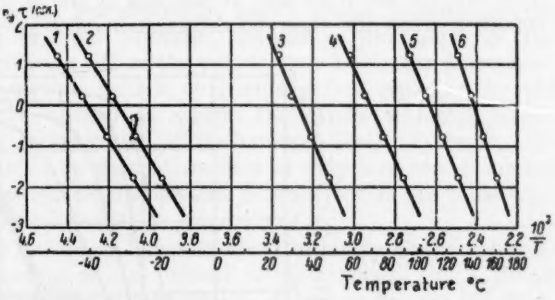

FIG. 11.—Relation between the time of relaxation of various polymers and the temperature.
1. Natural rubber with 3% sulfur.
2. Chloroprene.
3. Semivulcanized ebonite.
4. Methyl methacrylate with 30% plasticizer.
5. Methyl methacrylate with 10% plasticizer.
6. Methyl methacrylate without plasticizer.

as could be expected from the scheme. If the experimental curves in Figures 5, 6, 7 and 8 are described precisely by the equations given, then they can be used conveniently for determining the time of relaxation τ at different temperatures on the following basis: $\omega\tau \approx \sqrt{3}$,

$$|D| = \frac{D_{el\infty}}{2} \tag{11}$$

(disregarding D_{res}).

However, since the proposed scheme gives only the general relation and not its details, it follows that τ, determined according to this condition from the experimental curves, has only a limited, conditional meaning. Nevertheless, knowing its value at different temperatures, it is possible to judge the behavior of polymeric substances under different temperature-frequency conditions. The relation: $\log \tau = f\left(\frac{1}{T}\right)$ for the polymers investigated is given in Figure 11. The graphs show that, within a small temperature interval, straight lines in these coördinates are obtained, *i.e.*, the exponential law is followed:

$$\tau = Ae^{\frac{U}{kT}}.$$

Unfortunately the energy of activation cannot be determined precisely from the slopes of straight lines, because wider temperature intervals as well as simple amorphous substances give curves, *i.e.*, U depends on the temperature. In this case, as can be readily seen, the tangent coefficient is not equal to the magnitude $\frac{U}{k}$ log e (when the ordinates are logarithm scales, as is done here). These straight lines make it possible to determine, for a given frequency of force, the particular temperature at which the elastic deformation constitutes one-half of the complete deformation. To this end, $\tau = \frac{\sqrt{3}}{\omega}$ is calculated, and the corresponding abscissa in Figure 11 gives the temperature. Every dot on the plane of this graph corresponds to a definite temperature and frequency of force. The dots on the right and at the top of the straight line correspond to the condition when the observed deformation of a given polymer exceeds one-half

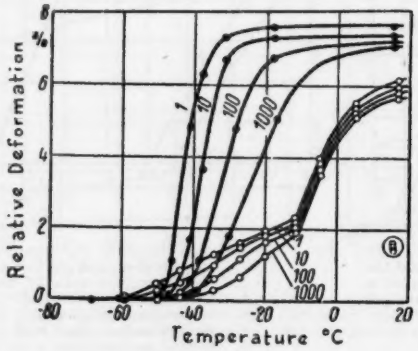

FIG. 12.

the complete deformation and, with increasing deviation of the point from the straight line, tends toward the value of the ordinary elastic deformation.

This discussion does not in the least cover all possible conclusions from the concepts presented here. In the scheme itself, no account is taken of the factors complicating the process, such as flow, the effect of fillers and the influence of the magnitude of the deformation. It should be noted that a decrease in the observed elastic deformation may be related not only to the gradual decrease in the probability of regrouping of particles at lower temperatures, but also to the discontinuation of regrouping because of crystallization. The problems related to crystallization processes in polymers have been widely investigated. The present discussion is confined to the presentation of the results of measurements of the dynamic treatment of spatial polymers, obtained by polymerization of chloroprene at room temperature, for a considerable length of time.

In Figure 12 two groups of graphs for this material are shown. The lower curves differ sharply from the usual behavior of the polymer. The specimen, which after a prolonged period of rest at room temperature forms centers of crystallization, becomes quickly crystallized when exposed to low temperatures; this leads to a rapid rise in modulus (without any evidence of dependence on frequency), to the appearance of turbidity, and to an increase in density. Tests showed that under these conditions the modulus can rise by several tens of times. At still lower temperatures the phenomena become dependent to a con-

siderable extent on the frequency, at the expense of the residual amorphous phase. When heated at room temperature this specimen showed a deformation which was considerably lower than the original values (dots surrounded by circles), *i.e.*, the crystalline phase formed failed to melt at room tempertaure. Heating at 60° C for 15 minutes caused complete recovery of the elastic properties. The top curves were plotted from the heated specimens; the interval of temperatures within which the maximum velocity of crystallization was measured was passed rapidly. The resulting picture shows a typical appearance characteristic of other polymeric amorphous materials. The object is to illustrate the relation between loss of elasticity and change of structure. As can be seen in Figure 12, the relations are widely different from those observed previously. These phenomena are very evident in natural rubber and chloroprene resins. In vulcanizates this second case is rarely observed at small deformations, but at high deformations by stretching (300 per cent and higher) it plays an important part. The relaxation phenomena of highly elastic deformation are similar to those of other oriented processes, because of the unity of the physical nature of these processes. Thus the polarization of dipolar amorphous dielectric substances in an electric field is qualitatively well explained by the Debye theory, which can be utilized to explain the nature of highly elastic deformations (except for a consideration of the internal field). Evidently, the phenomena of double refraction in the deformation of polymers and a number of other processes accompanying orientation can be described in the same way, but without limitation by small fields.

The kinetic theory of the nature of forces involved in highly elastic deformation, described in the beginning of the present article, explains, by a simple mechanism, the nature of highly elastic deformation. However, because investigators[1, 7] have not taken into account the forces of interaction between particles (they considered the ideal case), it has been impossible to deal with the actual character of the dependence of deformation on the temperature and the duration of the forces. The relaxation involved in the orientation and disorientation of highly elastic substances enabled Frankel[26] to develop the Mark theory with the aid of the concept of kinetics of the process by introducing the diffusion nature of the orientation process. Later Kuhn[27] pointed out the necessity of considering relaxation in the study of high elasticity. The material in the present work confirms the soundness of this view, and shows the resulting relations, which are highly important in the technique of elastic materials.

CONCLUSIONS

1. The proposed explanation of relaxation makes it possible to understand the general law of the dependence of deformation of highly elastic substances on temperature and frequency (time of action).

2. The results of measurements of various substances conform in a qualitative way to the scheme proposed.

3. With respect to mechanical losses, it is shown that application of the simple concept of relaxation makes it possible in many cases to explain the physical nature of the processes involved.

4. It is found that the relations characteristic of various relaxation processes, such as electrical and mechanical processes, are marked by a unity in their physical nature.

REFERENCES

[1] Meyer, Susich and Valko, *Kolloid-Z.* **65**, 208 (1932).
[2] Kuhn, *Kolloid-Z.* **76**, 253 (1936).
[3] Kuhn, *Naturwissenschaften* **24**, 22, 346 (1936).
[4] Kuhn, *Angew. Chem.* **48**, 258 (1936).
[5] Guth and Mark, *Naturwissenschaften* **23** (1937).
[6] Guth, *Kautschuk* **13**, 201 (1937).
[7] Mark, *Uspekhi Khim.* **8**, 69 (1939).
[8] Kobeko, Kuvshinskiĭ and Gurevich, *Bull. acad. sci.* (U. S. S. R.) **3**, 329 (1937).
[9] Howink, "Elasticity, Plasticity and Structure of Matter", Cambridge, **1937.**
[10] Stefan, *Wiener Ber.* **57**, 697 (1863).
[11] Ramsauer, *Ann. Physik* **30**, 417 (1909).
[12] Kats, "Rentgenografiya Kolloidov i Tkaniĭ", **1937.**
[13] Misch and Picken, *Z. phys. Chem.* **36**, No. 5-6, 398 (1937).
[14] Van Geel and Eymers, *Z. phys. Chem.* **3**, 240 (1929).
[15] Farwell, *J. Applied Phys.* **10**, 109 (1939).
[16] Holt and McPherson, *J. Research Natal. Bur. Standards* **17** (1936).
[17] Hetenyi, *J. Applied Mech.* **5**, 149 (1938).
[18] Howink, *Z. phys. Chem.* **183**, 3, 209 (1938).
[19] Frumkin, *J. Rubber Ind.* (U. S. S. R.) **10**, 400 (1936).
[20] Kosten and Zwicker, *Physica* **4**, 221 (1937).
[21] Roelig, *Kautschuk* **13**, 154 (1937).
[22] Mikhaĭlov and Kirilina, *J. Tech. Phys.* (U. S. S. R.) **8**, 19, 1723 (1938).
[23] Kornfel'd and Poznyak, *J. Tech. Phys.* (U. S. S. R.) **9**, 4 (1939).
[24] Roelig, *Kautschuk* **15**, No. 1, 7; No. 2, 32 (1939).
[25] Kosten, *Kautschuk* **15**, No. 3, 48 (1939).
[26] Frankel, *Acta Physiochim.* (U. S. S. R.) **9**, 2, 235 (1938).
[27] Kuhn, *Z. phys. Chem.* **42**, 1 (1939).

II. DYNAMIC METHOD OF STUDYING ELASTIC MATERIALS

Yu. S. Lazurkin

1. INTRODUCTION

Most articles made from elastic substances are intended for service under dynamic conditions. Static methods of investigation are clearly insufficient for determining the behavior of elastic substances under dynamic conditions and therefore there has for a long time been a need for dynamic tests. In recent years several dynamic tests have been developed, and a number of investigations of elastic properties under dynamic conditions have been published. The works of Frumkin[1], Roelig[2], Kosten[3], Naunton and Waring[4] and other investigators have established a series of relations in the behavior of elastic substances under dynamic conditions. However, the limited intervals of frequency and temperature in these experiments gave relations of peculiar character and even led to contradictions. Thus Naunton and Waring showed that, under dynamic conditions (at high frequencies), automobile tire casings act as solid hoops and, according to Roelig and Kosten, the relation between modulus and frequency, though still existing, is of relatively little importance. The development of a concept of the mechanism of highly elastic deformation, and in particular the disclosure of relaxation made it possible for Kornfel'd and Poznyak[5] and Mikhaĭlov and Kirilina[6] to demonstrate experimentally the existence of a more general law relating the phenomena. However, in their experiments, the frequency in both cases changed within narrow limits, and consequently these investigations too do not give a general picture of the behavior of elastic materials in relation to the frequency of deformation and temperature. The idea of highly elastic deformation, as well as that of relaxation, comes down to the fact that the magnitudes of the deformations observed depend on the relation between the time of action of the force and the time required for regrouping of the particles in the substance during the deformation. If the time of action of force t is shorter than the time of relaxation τ characterizing the velocity of rearrangement of particles, then highly elastic deformation has no time to take place, and the specimen behaves as a solid. Under the opposite condition,

highly elastic deformation does take place, and the material behaves as a typical highly elastic substance. At $t \geqslant \tau$ and $t \leq \tau$ the magnitude of deformation depends but little on t; but when $t \backsimeq \tau$, the dependence becomes very great. Hence the method must allow changes in action of force t or its frequency ω within wide limits. Since with all plastic substances the time of τ depends on the temperature, it is necessary also that the temperature of a specimen be regulated within wide limits. Aleksandrov and Gaev have constructed for our laboratory an apparatus which makes it possible to fulfill all these conditions.

2. APPARATUS AND METHOD

With this apparatus work can be performed at temperature intervals from −180° C to 200° C and at frequency intervals of 2000 to 1 vibrations per minute under the conditions of sinusoidal periodic load. The substance to be tested is subjected to vibration compression deformation by a force which changes with a given amplitude according to the sinusoidal law. The machine is fitted with a reversing device, with the aid of which it is also possible to study the elongation. Here, however, only compression is involved. The deformation changes according to the sinusoidal law (at sufficiently small deformations), remaining behind the force in phase, with an amplitude depending for a given substance on the modulus, frequency and temperature. The frequency is changed by the aid of a reductor, by means of which the desired frequencies can be obtained from the same motor. A drawing of the working parts of the machine is shown in Figure 1 and a general view in Figure 2.

The eccentric *1*, rotating at a given number of revolutions determined by the measured speed of the motor and the transmitting number of the reductor (equal to 1, 0.1, 0.01, 0.001) through creeper *2*, deforms spring *3*. The spring through spindles *4* and *5* presses specimen *6* fitted on table *7*. Spindle *4* is made of glass for thermal insulation of the lower part of the apparatus from its upper part. Table *7* with block *8* can be moved vertically by screw-nut *9* set in the lower orifice of tube *10*. All this is contained in brass cup *11*. Cup *11* and tube *10* are screwed into flange *12*, made of wood to ensure thermal insulation. The deformation of a sample is measured with the aid of mirror *13*, fastened to a steel prism. The sharp ribs of the prism fit into grooves on spring plates *14* and *15* perpendicular to the plane of drawing. Plate *14* is fastened to the lower part of spring *3*, and vibrates with it in the vertical direction at an amplitude equal to the amplitude of deformation of the specimen. In doing so, mirror *13* is turned around the axis, perpendicular to the plane of drawing, and reflects a beam of light on the scale set at a distance of 50 cm. In this manner the deformation of a sample is measured by the displacement of the light spot on the scale. The force is determined by the elasticity of spring *3* and the eccentricity of eccentric *1*.

The dependence of both force and deformation on time is shown in Figure 3. F_0 is the force of initial compression, F_1 is the doubled amplitude of the variable force, $\triangle l_0$ is the initial deformation, and $\triangle l_1$ is the doubled amplitude of variable deformation. The initial compression can be varied from zero to a maximum by moving supports *16* down to decrease the compression or up to increase the compression. The vertical distance between the supports, taken as constant, gives the final amplitude of deformation. The specimens are cylinders 5-14 mm. in diameter and 1-10 mm. in height. The specimens most frequently used measured 10-12 mm. in diameter and about 3-5 mm. in height. The temperature

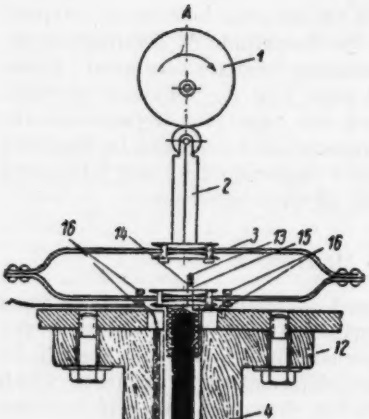

FIG. 1.

FIG. 2.

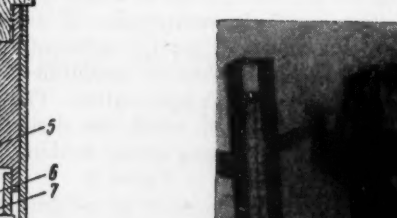

FIG. 3.

of a sample in experiments below room temperature was regulated by the depth of immersion of cup *11* in the Dewar flask filled with liquid air. In experiments at elevated temperatures, control is effected by varying the current in the electric furnace in which cup *11* rests. The temperature of the specimens was measured with thermocouple *17*. The pressure of eccentric *1* on spring *3* (Figure 1) creates the force which acts on the specimen. With an equal pressure of the eccentric, this force changes in close accord with the sinusoidal law, though differing from it in two respects. First, the movement of creeper *2* is not exactly sinusoidal, which becomes evident from the simple geometrical structure. However, as was shown by a graphic study, movement of the creeper at a given eccentricity differs so slightly from the sinusoidal that this small difference can be practically disregarded. Secondly, the elastic force of spring *3* depends on the mutual distance of its upper and lower halves, for it is governed not only by the displacement of creeper *2*, but also by the deformation of the sample in relation to the displacement of the lower half of the spring. To reduce the influence of this factor, the relation between the maximum displacement of creeper *2* and the deformation of a specimen must be sufficiently great. The motion of eccentric is 5 mm., and the doubled amplitude of deformation of the specimen does not exceed 0.25-0.30 mm. Hence the error introduced by deformation of the specimen is less than 5-7 per cent. When the specimen no longer deforms (with a decrease of temperature), the amplitude of the force increases by not more than 5-7 per cent. The law of change of deformation was checked experimentally by the following procedure. A cylinder, revolving uniformly around the axis parallel to axis *AB* (Figure 1) was placed in the path of a beam of light, reflected by mirror *13*, indicating the deformation. The beam of light produced markings on a photographic film covering the cylinder. The curves obtained in this manner proved to be very close in form to sinusoidal curves. At the lowest frequency (1 vibration per minute), these curves were obtained with the aid of a mechanical counter of seconds. The amplitude of the force was measured by simple loading of the spring *3* (with the screwed spindles *2*, *4* and *5*) and noting the relation between the elastic force and the bend. The experiments, described in the next chapter and also in the preceding article, were carried out at $F_0=1.2$ kg., $F_1=2.7$ kg. (Figure 3). Calibration of deformations was made with the aid of standard plates of given thickness. The plates were inserted in place of specimen *6*, and the measurements were made by the displacement of the light spot on the scale. The conversion coefficient obtained was 0.031 mm. deformation of the sample for each 1 cm. of the scale. The error in measuring the forces is 5-7 per cent; the absolute error in measuring the deformation is 0.003 mm. The absolute deformation of samples in the elastic state (with corresponding selection of their geometric dimensions) varies within the limits of 0.06-0.30 mm. The relative deformation varies within 0.5-20 per cent. When the sample has become solid, the deformation, recorded by the apparatus, becomes zero, because the device is not designed for the measurement of high moduli. Deformation of certain parts of the apparatus gives an additional motion of about 0.006 mm., which is deducted each time from the measured deformation. The true vibration frequency of the system lies above the upper limit of the applied frequencies, and when specimen *6* is replaced by a spring (Figure 1), the apparatus shows no relation between frequency and deformation. By controlling the temperature of the specimen, which is measured by two thermocouples connected with the top and bottom surface of the sample, it is found that with change of temperature at a rate of 1° C in 3-4 minutes the change of temperature in the sample does not exceed 0.5° C. In compression

tests, because of friction between the specimen and the supports, an uneven strained state is set up[7]. This results in too high values of the modulus of elasticity, which must be taken into account in comparing data obtained in stretching experiments. However, this does not offer difficulties in solving the problem by the proposed method, *viz.*, the investigation of the frequency and temperature dependence of deformation. Since the influence of the supports in which the specimen is compressed depends on the dimensions of the specimen, only specimens of nearly equal form and size should be used in all experiments. It should be noted that the time interval of the action of the force can be extended to prolonged durations by the following procedure. The eccentric is turned in such a way that the specimen is exposed to the action of a force from zero compression to a maximum. The deformation is then measured at the required intervals of time. These measurements are repeated at different temperatures. This procedure makes possible a method of conversion from the dynamic to static measurements.

3. CERTAIN PRACTICAL CONCLUSIONS

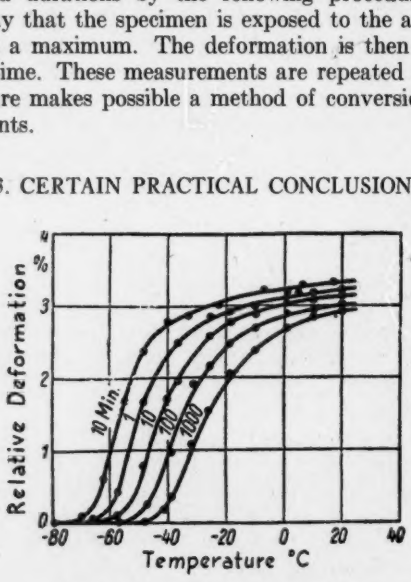

FIG. 4.—Relation between the deformation of rubber and the temperature. Parameter—frequency in vibrations per minute. The left-hand curve was obtained by the static method; the time of action of force was 10 minutes. Cylindrical specimens 2.4 mm. in height and 12 mm. in diameter.

Time of action (or frequency)	Temperature of semideformation
10 min.	— 55 to — 56
1 vibration per min.	— 48 to — 49
10 vibrations per min.	— 40 to — 41
100 vibrations per min.	— 32 to — 33
1000 vibrations per min.	— 24 to — 25

The graphs in Figure 4, obtained from natural rubber containing 3 per cent sulfur, show the relation between the relative deformation $\frac{\Delta l_1}{l_0}$ and the temperature at different frequencies and the time of action of force of 10 minutes (left-hand curve). (Data on the measurements of other polymers are given in the succeeding article by Gurevich and Kobeko). On the basis of the graphic data and curves of other polymers, the following practical conclusions can be drawn.

1. At room temperature, within a given interval of frequencies, the deformation (and consequently the modulus) of unloaded rubber depends but little on the frequency. A marked dependence on the frequency at room temperature can be expected for this material (on the basis of extrapolation) at frequencies of approximately 10^6 vibrations per minute.

2. The position of the region of rapid rise of modulus with decreasing temperature depends on the frequency. The temperature at which the deformation constitutes the semideformation at room temperature depends on the time or the frequency of action, as shown in the above table. When tested by the static method, rubber gives a semideformation at $-56°$ C; when tested at the frequency of 100 vibrations per minute and the same temperature it gives practically zero deformation. It follows that, for the characterization of articles resistant to cold and intended for service under dynamic conditions, it is impracticable to make use of the static method without taking into account the relation between deformation and time of action.

3. The temperature of hardening of rubber also depends on the frequency. Hence elastic articles, such as shock absorbers, under indefinite vibrating conditions at various frequencies, operate within corresponding intervals of temperatures as elastic substances at one frequency, whereas at another frequency at the same temperatures they act as hard, glass-like materials. Automobile tires, subject to service at frequencies of the order of thousands of vibrations per minute, show in service a lower resistance to cold than that determined by static tests. This difference may be 30-35° C. This is substantially true of conveyor belts, flexible sleeves, etc., which operate at low temperatures.

4. Since the relations which have been described are true not only of rubber but also of other polymeric resins, it follows that they apply qualitatively to plastic materials. Important consequences follow from the foregoing with respect to the thermal resistance of plastic materials (softening temperature). This temperature, like the temperature of freezing of rubber, depends on the time the force acts.

5. The results described are true not only of static and dynamic forces but also of impulse and impact forces. Measurements of various elastic materials make it possible to form a diagram of their behavior for different temperature-frequency conditions. To this end, records are taken of the relation between temperature and deformation for several durations of action, and of the temperature at which the half-deformation for each time of action is observed (*i.e.*, the deformation, constituting one-half of the final deformation, toward which the observed deformation approaches at sufficiently high temperatures). On this basis, the relation between the temperature of half-deformation and the time of action is constructed. If the reverse absolute temperature is plotted as abscissa and the logarithm of the time of action as ordinate, a straight line is obtained, as shown in Figure 5.

If, under periodic conditions, $1/\omega$ is the time of action (ω-round frequency) and under static conditions for the time of action of force, then, as shown by tests, the points in both cases lie on a straight line. (From the scheme given in the preceding article in this series, one should rather take for the corresponding durations of action the magnitude $\frac{\sqrt{3}}{\omega}$ or the time of action of force, multiplied by $\frac{\sqrt{e}}{\sqrt{2}} \cong 1.44$ (*cf.* Equations 5 and 11). Since, however, this scheme has only

qualitative significance, our method can be used as more convenient and practically no different). With the use of this straight line, it is possible to pass from one frequency system to another. With T_0 known, and the temperature of half-deformation at the time of action t_0 measured, it is possible to calculate the corresponding temperature of half-deformation for any other time of action t, according to the equation:

$$\log t_0 - \log t = B\left(\frac{10^3}{T_0} - \frac{10^3}{T}\right).$$

According to experimental evidence, this value for rubber is $B=8.2° \pm 0.3°$, if decimal logarithms are used on the left-hand side of the equation. By determining the temperature by the static method at a time of action of, *e.g.*, 10 minutes, at which temperature the resulting coefficient of resistance to freezing is 0.5, it is possible to calculate the corresponding temperature for other durations (or frequencies) of actions. For a rough estimate of the effect of frequency on

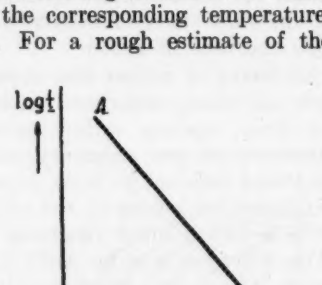

FIG. 5.

natural or synthetic rubber mixtures the following rule can be used. A ten-fold increase of frequency increases the temperature of half-deformation (the temperature at which the coefficient of resistance to freezing is equal to 0.5) by 5-7° C at slow deformations (of the order of seconds and minutes), and by 7-9° C at higher deformations (tenths and thousandths of one second).

REFERENCES

[1] Frumkin, *J. Rubber Ind.* (U. S. S. R.) **10**, 400 (1936).
[2] Roelig, *Kautschuk* **13**, 154 (1937); **15**, No. 1, 7; No. 2, 32 (1939).
[3] Kosten and Zwicker, *Physica* **4**, 221 (1937); *Kautschuk* **15**, No. 3, 48 (1939).
[4] Naunton and Waring, *India-Rubber J.* **96**, 22, 626 (1938).
[5] Kornfel'd and Poznyak, *J. Tech. Phys.* (U. S. S. R.) **9**, 275 (1939).
[6] Mikhailov and Kirilina, *J. Tech. Phys.* (U. S. S. R.) **8**, 19, 1723 (1938).
[7] Ariano, *Rubber Chem. Tech.* **11**, 561 (1938).

III. TECHNIQUE OF MECHANICAL TESTS OF VULCANIZATES OF RUBBER AND PLASTICS

G. I. GUREVICH and P. P. KOBEKO

INTRODUCTION

In a previous paper[1] we showed the existence of a fundamental relation in the elastic deformation of rubber mixtures and ebonite, as representatives of the class of highly polymeric substances. The basic features of that investigation are

as follows. For amorphous materials in general, the deformation of a loaded specimen consists of three components.

(1) A reversible initial deformation[2], which appears and disappears with the removal of the load, practically instantaneously. This common "visible" deformation, which is characteristic of solid materials in general, depends but little on the temperature.

(2) A reversible highly elastic deformation, which increases with time to a certain limit (practically equal, at a given load, at all temperatures)[3], *viz.*, complete elastic deformation. The time within which this limit is attained depends greatly on the temperature, *i.e.*, it decreases with increase in temperature, and *vice versa*.

(3) Plastic deformation, *i.e.*, irreversible flow of a substance under the action of a load.

With simple amorphous materials (monomeric and low polymerized substances), the viscosity drops rapidly when the material is heated, and the increase in the velocity of deformation under the action of a static load with increasing temperature takes place chiefly at the expense of an increased rate of irreversible flow in the substance. In contrast to this, with highly polymeric substances (including vulcanizates of rubber), the viscosity on reaching the temperatures at which the velocity of highly elastic deformation begins to increase rapidly remains very high, and the velocity of irreversible flow is, from a practical point of view, insignificantly low up to temperatures when the maximum rate of complete elastic deformation is reached. With polymeric substances, this complete deformation is very high, *e.g.*, for rubber stretched close to the limit of 1000 per cent of the original length; for polystyrene, about the same order; for polymerized vinyl acetate the reversible, highly elastic deformation can reach above 2000 per cent elongation. In the same communication the importance of the dependence of the velocity of increasing highly elastic deformation on the temperature was pointed out. To make this clear, we reproduce the graphs of the relations between the specific deformation of rubber and ebonite and the temperatures.

The same final deformation is reached at low as at high temperatures, but the lower the temperature the longer the time required for obtaining complete elastic deformation (the velocity of formation of complete elastic deformation increases with increasing temperature, in a rough approximation, according to the exponential law). In practice, measurements of the deformation at certain lengths of time give the total deformation, *i.e.*, the initial deformation (which is practically instantaneous) plus the highly elastic deformation during the observed length of time. The characteristic elastic properties of a polymeric substance can be shown by plotting the deformations for equal periods of time as a function of the temperature. Figure 2 shows on the same scale such curves for ebonite and rubber, constructed on the basis of graphs in Figure 1*a* and Figure 1*b*, for periods of time of 5 and 100 seconds (at the points of intersection of straight lines perpendicular to the axis of time with the curves of corresponding temperatures). It can be seen (Figure 2) that, with increase in the measured interval of time, the curves are shifted in the direction of lower temperatures, and *vice versa*. In Figure 2 the deformations are indicated by small circles, with the corresponding apparent moduli of displacement at the same temperature 5 and 100 seconds after application of the load. (By the apparent modulus, in distinction to the full modulus, is meant that magnitude which is inverse, not to the complete deformation, but to that part of the latter at the time of measurement). With longer and shorter intervals of time, the result-

ing apparent moduli will be correspondingly higher and lower. In limiting cases the initial and complete modulus is obtained. With change in temperature at a given time of measurement, the apparent modulus, as shown in Figure 2, also passes through all values from initial to complete. It follows that disregard of the initial deformation may lead to contradictory results in the determination of moduli, even with the same specimens of rubber or ebonite. This applies in varying degrees to other parameters used in characterizing the mechanical

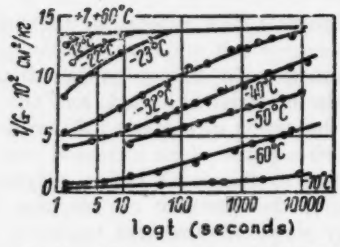

FIG. 1a.—Relation between deformation and time at different temperatures (for rubber).

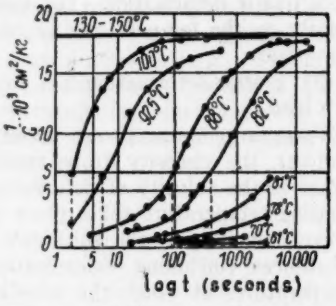

FIG. 1b.—Relation between deformation and time at different temperatures (for ebonite). The scale is 10 times greater than that in Figure 1A.

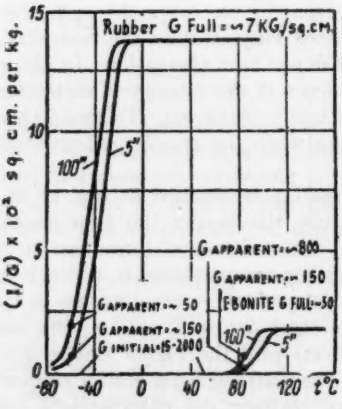

FIG. 2.—Deformation of rubber and ebonite recorded 5 and 100 seconds after the application of force.

properties of highly polymeric materials by different methods. All forms of mechanical testing or investigations deal, in the last analysis, with the deformation of the substance examined by a definite method and under definite conditions; hence a lack of correct understanding of the laws governing this deformation cannot fail to give faulty results. Examples of such errors are described below. In conventional methods of testing, the time relation of deformation is indirectly affected by the requirement of standardized procedures of operation[4]. However, when not based on a correct understanding of the processes of deformation, this standardization frequently leads to a situation where the experimental

results, obtained under conditions other than those specified, lose their significance and cannot be extrapolated to a general characteristic of the substance. Setting a definite interval of time of observation with an arbitrary standardization of experimental conditions results in an arbitrary division of the deformation into two parts, *viz.*, highly elastic deformation, fixed at the time of reading, is considered, without taking into account its specific behavior, as an instantaneous deformation; the residual part is either considered as viscous flow, which gives entirely arbitrary values of apparent viscosity, depending on the interval of time of measured deformation, or, what is equally arbitrary, the value is regarded as elastic after-effect. The inadequacy of conventional methods has been noted by many investigators[5]. However, attempts to improve these methods which are not based on the true law of deformation of highly elastic materials lead only to empirical characteristics of a given substance. As a matter of fact, experimental facts which appear to express specific individual properties of a substance often prove to be simply the result of a general law prevailing under the existing conditions, as is shown in Figure 1. In other words, these apparently specific individual properties can be frequently explained simply by the position and direction of curves of the type shown in Figure 2 within the corresponding temperature interval at intervals of measured time corresponding to service conditions. In any event, a knowledge of these characteristics is necessary in any investigation of the mechanical properties of polymeric substances. For a complete characterization of the elastic properties of a polymeric substance, it would be necessary to plot curves of the time relation of the final deformation at various temperatures (Figure 1). In actual practice it is possible to limit the procedure to several curves of the type in Figure 2, or at different intervals of measured time (with static load), or at different frequencies of the acting force (in accord with the conditions of dynamic tests). The latter method was developed by Aleksandrov, Gaev and Lazurkin[6] and Lazurkin[7]. The results of investigations can be found in the two papers. For elucidation only of the general law of changes in the elastic properties of a polymeric material by the action of certain factors, *e.g.*, vulcanization, the procedure can be confined to plotting curves of the temperature-deformation relation during unit time. In this communication, as well as in the earlier one, five seconds was chosen as the time. This makes possible a direct comparison of the results obtained and a rapid measurement by visual observation.

1

Measurements were made to determine the effect of time of vulcanization on the complete and initial deformations of a rubber vulcanizate and to establish the relation between temperature and deformation of ebonite specimens of various degrees of vulcanization. To this end, synthetic butadiene-rubber of various degrees of plasticity was mixed with 40 per cent of sulfur, but without any fillers. Different degrees of vulcanization were obtained by changing the time of vulcanization[8]. The method and apparatus described in the preceding article in the series were used; measurements were made of the static deformation by torsion, which at all the temperatures of investigation was fully reversible. The specific deformation[9], inverse to the apparent modulus of shift, was then calculated. The results, given in Figure 3, show that the initial deformation of all the vulcanizates is practically equal.

The initial moduli of displacement, corresponding to these deformations, are very close in magnitude for all the specimens studied (15,000-20,000 kg. per sq.

cm.). The complete deformation, however, decreases with increase in the time of vulcanization, *i.e.*, with increasing proportion of combined sulfur. Moreover, with increasing time of vulcanization the points of bending are shifted toward higher temperatures. The most probable explanation of this action of vulcanization is as follows. The velocity of reversible deformation of a polymeric substance is the velocity with which the macromolecules of a polymer can change their form, *viz.*, straighten out. The velocity of this straightening of the molecule under given conditions (load, temperature, etc.) is determined by its structural properties (mobility of its separate members, according to the kinetic theory),

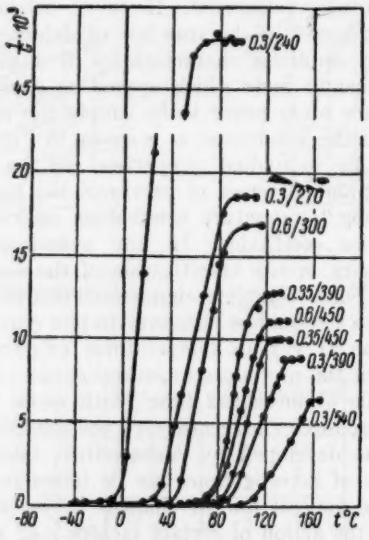

FIG. 3.—Temperature relation of deformation of 5 seconds of specimens of ebonite of different degrees of vulcanization. The denominator of the fractions indicates the plasticity; the numerator the time of vulcanization in min. Total sulfur 40 per cent.

and also by the conditions of its interaction with the neighboring molecules. With increase in size of the macromolecule, *e.g.*, with increasing polymerization, the number of its bonds (Van der Waals forces) with surrounding molecules increases and, all other conditions being equal, the process of forced and reversible change of its form is impeded. With increasing size of a macromolecule, its transposition as a whole is also impeded, and the latter results in an increase in viscosity. To retain the same velocity of deformation under constant conditions of action with increasing macromolecules and increasing velocity of deformation of the entire polymer, a great energy of thermal movement, *i.e.*, a great supply of heat, is required to overcome the increasing impeding forces. This determines the shift of the regions of bends of the deformation curves toward higher temperatures as a result of increasing degrees of polymerization. The chemical combination of sulfur with rubber during vulcanization can be regarded as a certain type of increased degree of polymerization: sulfur can link macromolecules of polybutadiene by residual double bonds into a macromolecule of greater size. The displacement of the curves in Figure 3 was brought

about in the same way as in the case of polymerization. The resemblance between polymerization and the action of sulfur is further confirmed by the fact that increase of hardness, *i.e.*, the degree of polymerization of the original product, runs parallel to the increase in the percentage of combined sulfur. The graphs in Figure 3 show that less plastic rubbers require shorter times for vulcanization to give curves of the same position as more plastic rubbers with longer times of vulcanization. In the case of linear polymers, an increased degree of polymerization should, in addition to the foregoing, increase the elasticity of the polymers, *i.e.*, its complete deformation (with increase in the number of members in the macromolecule, the final extensibility of the molecule increases). It follows that, if vulcanization is analogous to linear polymerization, an increase in the percentage of combined sulfur would increase the complete deformation (decrease the complete modulus). The graphs in Figure 3 show the reverse.

However, vulcanization is evidently a process analogous not to linear, but to spatial polymerization. Evidently sulfur forms bridges, displacing a part of the

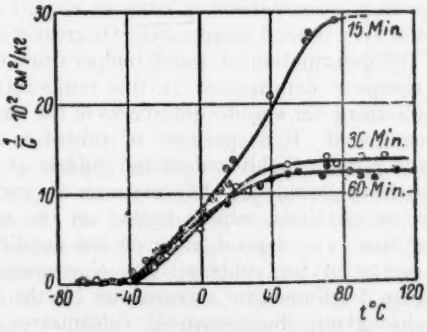

FIG. 4.—Temperature relation of deformation of 5 seconds for specimens of butadiene rubber, vulcanized 15, 30 and 60 minutes. Total sulfur 3 per cent.

chains of macromolecules (this supposition, as is known, is supported by many investigators), which connect the whole into a network structure and in this way decrease the final extensibility of a vulcanizate. The graphs in Figure 3 show this effect quite clearly. The complete modulus of shift increases with vulcanization. With increase in the percentage of combined sulfur, the modulus increases toward a limiting value which is governed by the free sulfur consumed, which, from a practical point of view, is the end stage of vulcanization. Further extension of the time of vulcanization has a progressively diminishing effect. In Figure 3, this process is not completed, and the complete modulus for a short time of vulcanization (9 hours) does not reach the final value. Further vulcanization brings about a noticeable increase of the complete modulus. With small contents of total sulfur, the process is completed much quicker. The graphs in Figure 4 show data for one kind of butadiene rubber, containing only 3 per cent of total sulfur, and vulcanized 15, 30 and 60 minutes. The curves for 30 and 60 minutes of vulcanization are very much alike; curve for 15 minutes is considerably higher. Thus it is possible, by measuring the complete modulus, to estimate the final stage of vulcanization; the plotting of curves can be used as a method for correlating the original plasticity of rubber with the time of vulcanization and thus obtaining vulcanizates with any desired elastic properties.

The graphs in Figures 2 and 3 show that changes in the time of vulcanization have practically no effect on the initial deformation. They show clearly the lack of significance of data obtained at room temperature in studying the high elastic properties of ebonite, and the necessity of orientation for complete elastic deformation, which characterizes the specific elastic properties of rubber vulcanizates. In connection with what was said in the introduction about the principal shortcomings of conventional methods of investigation of the mechanical properties of highly polymeric materials, the following must be noted in relation to rubbers. For the limiting states of vulcanization, *viz.*, ebonite and soft rubber, the deformations, measured within an interval of temperatures close to room temperature, are practically independent of the temperature and time, as can be seen in Figures 1 and 2. It should be noted that, whereas in the case of rubber at room temperature, complete elastic deformation, the most important parameter of its elastic properties, is measured, in the case of ebonite we deal only with a characteristic common to all hard materials, *viz.*, initial "visible" deformation, which does not define its special mechanical properties as a highly polymeric substance. It follows that a comparison of data on ebonite and rubber at room temperature has only a very limited significance. Of greater importance is a comparison of data on the deformation at room temperature of different types of rubber capable of complete deformation at this temperature, because in this case the values characterizing the specific differences of the various type of rubbers are measured and compared. If a specimen of rubber is measured below the room temperature (or a more highly vulcanized rubber at room temperature), then arbitrary relations between the deformations of various rubbers at the time of observation are obtained, which depend on the temperature and the measured interval of time, *i.e.*, depend more on the conditions of testing than on the specific properties of the rubbers. The characteristics of the type of curves shown in Figure 3 differentiate vulcanizates by their elastic deformation and their position throughout the system of vulcanizates, the extreme representatives of which are hard ebonite and soft rubber (Figure 2). Moreover, the relations shown by these graphs make it possible to understand the results obtained with changes in experimental conditions or in the properties of a given substance.

2

As an illustration of the errors arising from a lack of knowledge of the peculiarities described above, the elastic deformation of highly polymeric substances, particularly of ebonite, the work of Church and Daynes[10] on the plastic deformation of ebonite can be cited. These authors carried out a systematic investigation of ebonite and methods of testing it. They showed that "the flow of ebonite under the action of a load increases greatly with increasing temperature", and undertook the problem of improving the method of studying this flow. In their experiments a specimen of ebonite in the form of a plate (placed in a water thermostat) was clamped at one end in a stationary holder, was twisted at the other end at an angle of $\alpha_0=20°$, and was held in this position for one minute, after which the specimen was released. Two minutes after release, the residual angle α was measured and expressed as percentage of the original angle of torsion.

Curves of the "percentage residual deformation" of specimens vulcanized for different times (taking only graphs of one kind of ebonite studied) are reproduced. Contrary to the findings of the authors of the work cited, these curves do not express plastic deformation and its dependence on temperature, because,

within the interval of temperatures studied, it is practically equal to zero. The explanation of the entire course of curves and the presence of maxima is as follows.

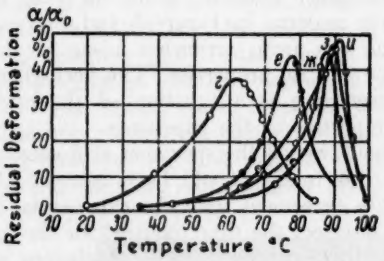

FIG. 5.—Residual deformation of ebonite, according to Church and Daynes.

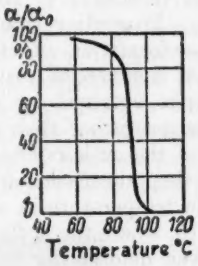

FIG. 6.—Deformation remaining 5 seconds after the load was removed, in percentage of the preliminary set deformation. (Preliminary set deformation is formed by the same load during different periods of time, depending on the temperature of test.)

The magnitude represented in Figure 5 as residual deformation, not fully resolved in 2 minutes, is the reversible highly elastic deformation created by torsion of the sample. At the lowest temperatures, indicated by the lowest point on the curves, at the left-hand side, the velocity of highly elastic deformation is so low that the specimen during the time of twisting has no time to undergo any marked highly elastic deformation. All torsions at an angle of 20° are produced by ordinary "visible" deformation, which requires a correspondingly great force. Complete deformation appears and disappears practically instantaneously by application and removal of the force. At higher temperatures the torsion of a sample at an angle of 20° requires a smaller force for the same speed of twisting, and the initial deformation, proportional to this force, is correspondingly smaller at the expense of the highly elastic deformation during the time of twisting, giving with the initial deformation the sum of the same torsion of 20° angle. When the torsion is released, only the initial deformation disappears instantaneously; the highly elastic deformation fails to relax completely in the two-minute period, and is defined by the authors as the residual deformation. With increase in temperature, an increasingly greater part of the preliminary torsion at an angle of 20° results from the highly elastic deformation, and a correspondingly smaller part from the instantaneously recovered initial deformation. This explains the formation of an increasingly greater residual deformation with increase in temperature (that part of the highly elastic deformation which failed to resolve in the two minutes). The maxima in Figure 5 are explained by the fact that the moment is reached when the increase of part of the elastic deformation in the total preliminary torsion (at an angle of 20°) begins to be accompanied by such an increase in velocity that in the period of two minutes an increasingly greater part is relaxed.

Within the temperature limits when complete elastic deformation appears and disappears practically instantaneously, zero residual deformation is again attained. A correct idea of the general laws of elastic deformation of highly polymeric substances makes possible a true understanding of the results ob-

tained by special methods, *e.g.*, such as the method described in the work cited. Uncritical use of the conventional concepts led the authors of the work cited and a number of other investigators in this field to construct special graphs and empirical, special laws for each substance studied (as in the case cited for ebonite). Proceeding from the curve maxima in Figure 5 and the concept of plastic deformation of ebonite, one can form erroneous ideas of the possibilities of commercial uses of ebonite and its properties. The very character of the graphs obtained by such a procedure is a function of the methods of investigation rather than of the properties of the substance.

Thus if the authors cited above had twisted the specimen at a constant force to 20°, then the time required for this torsion would have decreased with increase in temperature in approximate agreement with the exponential law (see Figure 1*b*, where the dotted curves intersect the time required for the formation of a given deformation at different temperatures). In an analogous way, the time of reversible relaxation, which is a maximum at low temperatures and decreases at higher temperatures, would change. Plotting the residual deformation 2 minutes after removal of the force would result at lower temperatures in the maximum residual deformation, decreasing with increase in temperature as in the curve of the type shown in Figure 6, a paradoxical "regularity" would in turn have been obtained, *viz.*, a decrease in the residual deformation, *i.e.*, an increase in viscosity with temperature. The curve in Figure 6 was derived from from Figure 1*b* by deducting from the given deformation S (at constant force) its parts obtained for the first 5 seconds at the corresponding temperatures, and by plotting the percentage of the remaining part as a function of the temperature. It is evident the method of investigation, without an understanding of the processes involved, cannot give correct results[11]. The literature shows many instances of similar erroneous attempts to derive special laws for a number of substances, based on attempts to force a new phenomenon into the scheme of conventional concepts of elastic and plastic deformation. As an example should be mentioned work on the deformation of synthetic resins[12], which in its errors (and the appended curves with maxima) is analogous to the work cited above and, therefore, requires no further comments[13]. With respect to synthetic resins and socalled plastic materials in general, a more detailed discussion is in order.

3

Especially when dealing with plastic materials, application of the laws of ordinary solid materials to highly polymeric substances, to which class many plastics belong, proves to be erroneous. The mistaken concept of flow, which in reality is predominantly the process of formation of a limiting deformation, is clearly illustrated photographically in Figure 7.

On the right-hand side of the photograph is shown a polystyrene bar *3*, moulded under pressure for testing thermal stability. The usual understanding of processes involved in moulding is based on the idea of plastic changes of form by flow under pressure at a particular temperature. However, moulded specimens on heating recover to a considerable degree their original form. Specimens *1* and *2*, of the same form as specimen *3*, were heated at 150° C for 20 minutes. Bar *1* was moulded from polystyrene polymerized in a test-tube; bar *2* was moulded from separate pieces of polystyrene, which on heating disintegrated into fragments, resembling in shape the original pieces. The results show that the deformation of polystyrene in this case is to a great extent reversible[14]. During moulding, highly elastic deformation takes place and this is retained on

cooling, because at room temperature the velocity of reversible deformation of polystyrene is insignificantly small. The time during which one-half of the complete elastic deformation of polystyrene would appear or disappear at room temperature is of the order of hundreds of thousands of years. At temperatures higher than 100° C, the constant of time is measured in seconds, and polystyrene returns rapidly to the original form. With polymeric plastics, whose noticeable increase in elastic deformation appears at temperatures somewhat above the room temperature, reversible deformation may reach a magnitude of practical importance in a comparatively short time; this magnitude increases with rising temperature. This explains the appearance of constant deformation (buckling and shrinking) of moulded articles of various plastic materials. To

FIG. 7.—3 is a polystyrene bar, moulded under pressure for tests of thermal stability. 1 and 2 are the same bars of polystyrene after heating at 150° C for 80 minutes.

make certain the stability of such a product at a definite temperature in service, it is necessary to know the time constant at this temperature. This can be obtained by constructing curves of the type shown in Figure 2, with time and method of loading adapted to the particular problem as parameters. Ordinary technical tests of thermal stability and brittleness also require a critical revision, with account being taken of the true mechanism of deformation.

Original plasticity	Time of vulcanization (min.)	Thermal stability (°C)
0.30	240	Bends at < 20
0.30	270	Bends at < 20
0.30	390	Bends at 74
0.30	540	Bends at 80
0.35	390	Bends at 70
0.35	450	Bends at 75
0.60	300	Bends at $<<20$
0.60	450	Bends at 72

(Data obtained by the Lebedev Works of Synthetic Rubber.)

The table above shows tests, by the Martens method, of the thermal stability of the vulcanizates used in plotting the curves in Figure 3. From these

data it is impossible to obtain characteristics of separate vulcanizates. The results suggest a division of the vulcanizates into two groups: (1) specimens bending strongly with the initial rise of temperature, and (2) specimens bending more slowly and characterized by the temperature at which bending reaches a conditional value. The lower regions of the incline of the curves of specimens of the first group, as shown in Figure 3, lie more to the left of 50° C, and for the second group more to the right of 50° C. In other words, vulcanizates, whose deformation in 5 seconds begins to increase rapidly at temperatures below 50° C belong to the thermally unstable groups; vulcanizates, whose deformation begins to increase rapidly above 50° C belong to the group of ebonites of various thermal stability. It should be noted, however, that since tests by the Martens method show only the initial stage of increasing deformation (the deformation at the very beginning of bending), the difference in the thermal values at which a given standard bend is reached is very small (they correspond roughly to the segment of initial bifurcation of the curves, lying above 50° C, as in Figure 3). This explains the very limited accuracy of measurements of

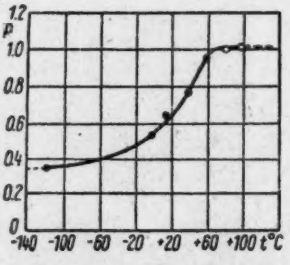

FIG. 8.—Thermal relation of work expended by the plunger in shearing and deformation of specimens of ebonite. The full reserve of work of plunger is taken as a unit.

thermal stability of various grades of ebonite. The actual difference in their properties, sharply revealed by the complete deformation and the character of curves (Figure 3), does not agree with the data on thermal stability. In the most favorable cases, measurements of heat stability indicate the boundary between the two groups of vulcanizates with different thermal characteristics. Secondly, the bend of a bar is explained by the concept of flow. However, bent bars can easily be returned to their original state by removing the load and heating. Therefore measurements of thermal stability may not show any flow, except for substances of low molecular weights, where a sharp bend is associated with a decrease in the macroscopic viscosity of the specimen and indicates the possibility of its destruction. With ebonite, polystyrene[15] and similar polymeric substances, the observed "flow" indicates only the velocity of complete deformation and does not indicate an approach to destruction. Under certain conditions in general practice, where small deformation is permissible, the rejection of manufactured articles on the basis of the Martens test may prove unprofitable (ebonite products under small loads are capable of service at temperatures up to 140° C, if the load and corresponding complete elastic deformation do not exceed certain limits.

Third, the Martens method of testing is highly arbitrary. The resulting data can, in general, be used in commercial practice only under certain conditions

where articles are bent under conditions similar to those in the Martens tests. But even in this case data by the Martens test may be useless, because a specimen, known to be thermally stable, nevertheless reaches the critical point of bending after a long time. At 50-70° C, *i.e.*, at temperatures below those in the table of heat stability of the vulcanizates investigated here, the characteristic bend can be effected without a further increase of temperature by holding for several seconds or minutes, so that practically in the initial stage of bending their behavior does not show any difference. It follows that the significance of results obtained by the Martens method is extremely limited, particularly in the absence of a correct understanding of the relations involved in the bending of the specimen. A proper interpretation of the foregoing discussion makes it possible not only to avoid errors in evaluating the results, but also to utilize more rationally the resulting data. A more radical improvement would be to plot curves of the type in Figure 3 (with corresponding intervals of time and frequencies of application of the force, depending on the practical problem involved), which show the entire behavior of the specimen. It should be noted here that the curves in Figure 3 characterize a corresponding vulcanizate with such uniformity that it is possible to obtain specific curves for a given specimen. The corresponding methods of testing will in many cases prove to be not much more complicated than the Martens method. In developing the method of static testing, use can be made of an apparatus analogous to the Martens device, taking the bending values at different temperatures at one interval or several intervals of time. (After each measurement, the specimen is unloaded and brought to its original form by heating). In addition to thermal stability, brittleness[16] is one of the most common parameters used in technical tests of ebonite. In tests of the brittleness of highly polymeric substances, as in tests of thermal stability, certain relations appear which are different from those characteristic of ordinary solid materials, and the application to them of conventional ideas of brittleness and elasticity is wrong. The graph in Figure 8 shows the general relation between the temperature and the work expended in destroying specimens by the Sharpe apparatus for one type of ebonite from synthetic rubber. The graph represents the mean experimental values of eight specimens. The mean values of the data of the eight specimens were obtained at each temperature. Because of considerable variability in this method, the exact statistical value of the mean magnitude can be obtained only by means of a large number of observations at each temperature. However, the general character of the relation can be observed directly at temperatures above room temperature. With increasing temperature the degree of bending of the specimen on impact increases and the height of elevation of the plunger correspondingly decreases after crushing. The top segment of the curve shows the temperatures at which the specimen remains unbroken and the plunger is either stopped or forced back. The general relation represented by this curve can probably be explained in the following manner. The change in quantity of work is related fundamentally to the change in magnitude of the highly elastic deformation before destruction of the specimen. In the case of metals, the transition to plasticity is related to a sharp increase in the quantity of work, registered by the Sharpe apparatus, which is chiefly expended in plastic deformation. In the present case, an increase of temperature increases the work expended in highly elastic deformation. At lower temperatures, the deformation is small. This deformation is followed by destruction. With increasing temperature, deformation is accelerated, and at the corresponding speed of bending of the specimen, the entire energy of the plunger is expended in overcoming the elastic drag,

whereby the specimen bends, without destruction, and returns together with the plunger. Figure 8 shows that, even if the entire work at room temperature is assumed to be expended on destruction of the brittle specimen (which is erroneous), the work of reversible deformation with increasing temperature may become predominant. The relation between deformation and destruction requires special investigation. Here it should be noted only that the extremely sharp ascent of the curve, characterizing the transition from the state of brittleness at room temperature to the state at which ebonite does not break (at 80° C under the conditions in this investigation), but is reversibly bent on impact, lies within the interval of working temperatures of ebonite. A drastic change in the extent of bending with a slight change of temperature cannot be without an effect on the utility of ebonite, *e.g.*, in mechanical service. Even if the qualitative values of the "work of destruction" at room temperature proves to be useful, *e.g.*, in the sorting of products[17], the relation between industrial properties and impact effects can be learned only from the deformations under controlled conditions, depending on the temperature, with due regard for the general law of elastic deformation. This method, which is analogous to the procedure of Aleksandrov and Lazurkin, is well adapted to a number of cases involving simple conditions, *e.g.*, measuring bending at impact load in relation to temperature and velocity of action, with regard to the relations defined here. The method makes it possible to evaluate various types of products and their utility under specified service conditions.

CONCLUSIONS

1. From the point of view of mechanical properties, the special attributes of highly polymeric substances, including rubber vulcanizates, are clearly defined by their reversible highly elastic deformation as a function of time. The time required for attaining this deformation within a given interval of time varies practically from zero to infinity.

2. Disregard of the temperature and time relation of deformation of highly polymeric substances leads to erroneous conclusions regarding their industrial working properties, and is the cause of the unsatisfactory results obtained by conventional methods of investigation.

3. The effect of increased degree of vulcanization on the mechanical properties of rubber is manifest in a decrease in complete elastic deformation and shift of the temperature-apparent modulus (inverse to the deformation in a given time) curve toward higher temperatures.

4. Conventional ideas of the plastic (irreversible) and elastic deformation of solid materials, when applied to highly polymeric substances without concern for the laws governing their deformation, lead to erroneous conclusions regarding the existence of specific properties of individual substances, *e.g.*, ebonite and synthetic resins, and mistaken hypotheses regarding structural changes during their deformation. In the present communication, this is illustrated by studies of various investigators[10, 12, 18].

5. Conventional methods of studying thermal stability and brittleness, as well as other methods of testing, of highly polymeric substances frequently do not make it possible to evaluate the actual technical utility of materials within intervals of temperature encountered in service and they should be critically reëxamined with regard to the relations between deformation and reversibility, time and temperature.

6. In moulding highly polymeric plastics under pressure, it is necessary to consider the highly important, and in some cases predominant, part played by highly elastic reversible deformation of the total deformation, which is capable of becoming very pronounced with time and with increase in temperature.

REFERENCES

[1] Kobeko, Kuvshinskil and Gurevich, *Bull. acad. sci.* U. R. S. S. **3**, 329 (1937).

[2] By reversible deformation is meant, in distinction to irreversible or plastic deformation, the deformation which, after removal of the deforming force, at which the specimen returns to its original form.

[3] Throughout this discussion secondary effects are not considered, since they are but little pronounced compared with the fundamental effects of elastic deformation; in particular the effect of a certain increment of the complete modulus of elasticity of rubber, with increasing temperature—an effect of great importance in the kinetic theory of elasticity. With the arrival of complete deformation under a static load, a slow, relatively small increment of deformation with time at a given temperature is also observed.

[4] Dawson and Porritt, "Rubber: Physical and Chemical Properties", Croydon, **1935**, 211.

[5] Behre, *Proc. Rubber Tech. Conference*, London, **1937**.

[6] Aleksandrov, Gaev and Lazurkin, *J. Tech. Phys.* (U. S. S. R.) **9**, 1249 (1939).

[7] Lazurkin, *J. Tech. Phys.* (U. S. S. R.) **9**, 1261 (1939).

[8] All specimens were prepared at the Lebedev Synthetic Rubber Works in a study of the properties of ebonite by several investigators. The results of the laboratory investigation are incorporated in this work. The writers wish to express their gratitude for the assistance rendered.

[9] Since, with polymeric substances, deformations in a given time are not proportional to the load, the apparent "moduli of shift" and the inverse "specific deformations" themselves depend to a certain degree on the load and form of the specimens. The graphs in Figure 3 show the deformations of cylindrical specimens, with the working part 4 cm. in length and 0.8 cm. in diameter at the moment of twisting (1 kg. per cm.).

[10] Church and Daynes, *J. Research Assoc. Brit. Rubber Mfrs.* **5**, 11 (1936).

[11] It is of interest that in 1932 Church and Daynes[10] obtained curves for ebonite analogous to our curves in Figure 1*b* and Figure 2 (for ebonite). (cf. a paper by Porritt at the London conference on rubber)[18]. Porritt shows this to be a method of determining initial plastic deformation, and he regarded the curves as representing a special property of the elastic and plastic deformation of ebonite. No conclusions were drawn as to the actual law of deformation of ebonite as a representative of polymeric substances. The curves of maximum residual deformation (Figure 5) obtained by Church and Daynes much later are considered by Porritt, not to be related to the law which also characterizes the curves in Figure 1*b* (and is most simply expressed by them), but as a new manifestation of the plastic-elastic properties of ebonite, *viz.*, a result of the existence of two phases, one of which liquifies. The conclusions of Porritt in the work cited demonstrate to what arbitrary and erroneous conclusions one is led when one fails to understand the true laws governing the mechanical deformation of polymeric substances.

[12] Erk and Holzmuller, *Physik Z.* **39**, 559 (1938).

[13] It should be noted that, in this case, depending on the temperature and the structure of individual resins, the process of plastic flow affecting the character of resulting curves of residual deformation should also be taken into account. The most characteristic feature in the work[12] cited is the differentiation between the reversible and plastic components of deformation: the reversible part is only instantaneous deformation and all the remaining part is plastic deformation. From this follows the erroneous explanation of the resulting graphs (Figures 9 and 10 in the work cited), which in reality represent the time reversible deformation relation by introducing the additional factor of further condensation and polymerization.

[14] It is not possible, however, to disregard the flow of linear polymers, in distinction to spatial polymers and highly vulcanized rubbers, whose flow is from a practical point of view close to zero. However, polystyrene (a linear polymer) shows plastic flow, which becomes evident after a considerable time of application of the force and at sufficiently high temperatures.

[15] With the reservations made above. Cf. the footnote.[13]

[16] All that has been said regarding tests of thermal stability is applicable (with due regard to other conditions of load, method of action, etc.) to the Shore hardness test as well as to other analogous tests.

[17] This is highly doubtful, and could well be the subject of special investigation; *e. g.*, by plotting curves, analogous to those shown in Figure 8, for two types of rubber, *viz.*, natural rubber ebonite with normal brittleness, and synthetic rubber ebonite, whose brittleness, as is known, is different from the usual requirements. Here such shortcomings of the Shore apparatus as the immense scattering of data, and the dependence of the data on the slightest changes in standard conditions and a number of secondary factors, are disregarded.

[18] Porritt, *Proc. Rubber Tech. Conference, London*, **1937**.

VULCANIZATION OF RUBBER COMPOUNDS

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EFFECT OF HYDROGEN SULFIDE ON THE RATE OF VULCANIZATION *

Many articles in the literature give theories of the vulcanization of rubber; some have claimed that the formation of hydrogen sulfide during the cure is essential, others have denied the formation of any hydrogen sulfide during soft rubber vulcanization. In 1923 Bedford and Gray[2] presented a summary of previous theories and stated that hydrogen sulfide is liberated during vulcanization; it then reacts with zinc oxide present to form zinc sulfide. They further state that the accelerating actions of zinc dithiocarbamates are retarded by hydrogen sulfide. In 1936 Fisher and Schubert[4] stated that their data "appear to show that in the formation of hard rubber, when the amount of sulfur mixed with the rubber is approximately the theoretical (32.02 per cent) it adds to the rubber hydrocarbon until saturation is complete; very little, if any, substitution takes place". If, then, saturation with sulfur must be complete before substitution can take place, little or no hydrogen sulfide can be formed during soft rubber vulcanization. In 1939 Fisher[3] proposed a new theory of vulcanization, the basis of which is that hydrogen sulfide adds to the double bond of rubber to form a mercaptan.

Should this theory represent the actual mechanism of the vulcanization process, then the addition of hydrogen sulfide to a compounded stock should increase the rate of vulcanization and possibly produce an improved vulcanizate. Therefore, the tests which form the basis for this paper were carried out to determine the effect of hydrogen sulfide on the rate of vulcanization of accelerated rubber compounds.

The rubber compounds used in these tests were milled, vulcanized, and tested according to the specified procedure given by the A. S. T. M.[1] The uncured compounds were divided into two portions, and from each portion sheets were prepared (4.5×16.5×0.25 cm.). Half of the sheets were placed on shelves of 1-cm. wire screen in a closed drum, and hydrogen sulfide was passed through. In most cases the time of treatment was 15 hours at room temperature (25° C), which was sufficient to saturate the rubber compounds. Also tests were carried out in which the time of treatment was varied from 2 to 72 hours and the temperature from 25° to 100° C. To obtain reproducible results, the treated sheets must be vulcanized immediately after treatment because of the rapid loss of hydrogen sulfide on standing.

Table I shows the results obtained with rubber compounds containing practically every commercial type accelerator, many of which are used in combination with diphenylguanidine. All are retarded in rate of vulcanization by the hydrogen sulfide treatment. However, the physical properties of a majority of the compounds are not permanently affected; that is, a longer time of vulcanization of the treated compounds has produced maximum modulus and tensile figures

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comparable with the untreated compounds. Aldehydeamines, dithiocarbamates, thiuram sulfides, and litharge are permanently affected; that is, the maximum modulus and tensile figures obtainable are markedly poorer than those of the untreated compounds.

The ratio of mercaptobenzothiazole to diphenylguanidine in the last three compounds in Table I is that required to produce the diphenylguanidine salt of mercaptobenzothiazole. According to Bedford and Gray[2], hydrogen sulfide reacts with benzothiazyl disulfide (and presumably with other mercaptobenzothiazole derivatives such as benzothiazyl thiobenzoate) to give free mercaptobenzothiazole, which then forms a salt with diphenylguanidine. The results obtained with the treated portions of these compounds show no evidence of any such reaction. In addition to the tests shown in the table, one sheet of these treated compounds containing benzothiazyl disulfide, diphenylguanidine, or benzothiazyl thiobenzoate was placed in a vacuum oven for 2 hours at 25° C; curing produced the same modulus and tensile figures as the untreated portions. This is further evidence that these accelerators did not react with the hydrogen sulfide.

Table II shows the effect of varying the time and temperature of hydrogen sulfide treatment on the physical properties of the stock, together with variations in the weight of gas absorbed. The cure test results show that the retardation of the rate of vulcanization is least after 4-hour treatment at 25° C, is slightly more after 4 hours at 50° to 60° C, and is the maximum after 15 hours at 25° C. Likewise, the percentage increase in weight of gas absorbed shows that more hydrogen sulfide was absorbed after 4 hours at 50° to 60° C than after 4 hours at 25° C; but 15 hours at 25° C showed the maximum hydrogen sulfide absorption, which was approximately one per cent. In other words, the greater the absorption of hydrogen sulfide, the greater the retardation. Tests with rubber showed a one per cent increase in weight due to 15-hour hydrogen sulfide treatment at 25° C. Vulcanization in an atmosphere of hydrogen sulfide (1.75 kg. per sq. cm.) indicated that all accelerators were retarded permanently.

The results in Table III prove that no appreciable amount of zinc sulfide is formed as a result of the hydrogen sulfide treatment, since the increase in weight is approximately the same for a stock containing 10 per cent zinc oxide as it is for pure rubber. Comparison of the B and C compounds shows that there is no reaction between hydrogen sulfide and sulfur; doubling the sulfur content has not appreciably affected the retarding action due to hydrogen sulfide, because the maximum modulus and tensile figures are obtained in 120 minutes in each case. Comparing the physical properties of the D compound after hydrogen sulfide treatment with the physical properties of the untreated E compound shows that the former still contains sufficient zinc oxide to activate the accelerator. This result indicates that there is little reaction between hydrogen sulfide and zinc oxide.

The results in Table IV together with the three tread compounds (A, B, C) in Table III show that hydrogen sulfide treatment of these compounds has permanently retarded vulcanization, owing to the larger amount of absorbed gas, which is approximately 70 per cent more than for rubber. This retardation is not specific to any one accelerator. The vulcanized sheets of the treated compounds in each case showed porosity, and within a few hours after vulcanization showed a sulfur bloom.

The data in Table V show that the rate of combination of sulfur with rubber is retarded by the presence of hydrogen sulfide in the compound. They also

TABLE I

EFFECT OF HYDROGEN SULFIDE ON THE RATE OF VULCANIZATION OF RUBBER COMPOUNDS CONTAINING ACCELERATORS

(Formula: rubber 100.0, zinc oxide 10.0, sulfur 3.0, stearic acid 0.5, accelerator as shown; H_2S-treated 15 hours at 25° C.)

Accelerator		Untreated			H_2S-Treated		
		Max. modulus	Max. tensile	Vulcanization time	Max. modulus	Max. tensile	Vulcanization time
Name	% on rubber	(Kg. per sq. cm.)		(Min.)	(Kg. per sq. cm.)		(Min.)
Mercaptobenzothiazole	0.75	95	227	60	78	191	180
Benzothiazyl disulfide	1.00	118	235	90	106	219	240
Zinc mercaptobenzothiazole	1.00	98	228	90	92	217	240
Dibenzothiazyl dimethylthiolurea	1.00	118	214	90	95	218	240
Benzothiazyl thiobenzoate	1.00	109	221	90	88	218	240
Cyclohexylaminothiobenzothiazole	0.50	102	337	90	85.5	257	180
Diphenylguanidine	0.75	98.5	237	90	86	207	180
Reaction product of butyraldehyde and butylideneaniline	0.50	282	309	90	109	251	240
Tetramethylthiuram disulfide	0.25	256	305	45	60	192	120
Pip-Pip (piperidine salt of cyclopentamethylene dithiocarbamic acid)	0.25	264	335	30	100	148	120
Reaction product of carbon disulfide and methylenedipiperidine	0.25	231	321	30	100	197	120
Litharge (6.5% sulfur)	10.0	221	299	60	75	156	180
Benzothiazyl disulfide	1.0	137	350	45	121	283	180
Diphenylguanidine	0.25						
Mercaptobenzothiazole	1.00	141	336	45	119	306	180
Diphenylguanidine	0.25						
Zinc mercaptobenzothiazole	1.00	117	333	45	104	262	180
Diphenylguanidine	0.25						
Cyclohexylaminothiobenzothiazole	0.50	153	342	45	135	321	90
Diphenylguanidine	0.50						
Dibenzothiazyl dimethylthiolurea	1.00	111	333	45	105	302	180
Diphenylguanidine	0.25						
Mercaptobenzothiazole	0.44	151	352	60	144	315	180
Diphenylguanidine	0.56						
Benzothiazyl disulfide	0.44	154	352	60	119	350	180
Diphenylguanidine	0.56						
Benzothiazyl thiobenzoate	0.71	131	338	60	126	306	180
Diphenylguanidine	0.56						

TABLE II

EFFECT OF TIME AND TEMPERATURE OF HYDROGEN SULFIDE TREATMENT

(Formula: rubber 100.0, zinc oxide 10.0, sulfur 3.0, stearic acid 0.5, accelerator as shown; temperature of vulcanization, 134° C.)

Accelerator		Untreated			H_2S-Treated											
					4 hrs. at 25° C				15 hrs. at 25° C				4 hrs. at 50-60° C			
Name	% on rubber	Max. modulus (Kg. per sq. cm.)	Max. tensile (Kg. per sq. cm.)	Vulcanization time (Min.)	Max. modulus (Kg. per sq. cm.)	Max. tensile (Kg. per sq. cm.)	Vulcanization time (Min.)	Increase in wt.[a] (%)	Max. modulus (Kg. per sq. cm.)	Max. tensile (Kg. per sq. cm.)	Vulcanization time (Min.)	Increase in wt.[a] (%)	Max. modulus (Kg. per sq. cm.)	Max. tensile (Kg. per sq. cm.)	Vulcanization time (Min.)	Increase in wt.[a] (%)
Mercaptobenzothiazole ...	0.75	95	226	60	93	212	120	0.315	78	191	180	0.97	88	212	150	0.72
Benzothiazyl thiobenzoate.	1.00	109	220	90	106	218	120	0.318	88	218	240	1.01	97	219	180	0.78
Dibenzothiazyl dimethyl-thiolurea	1.00	119	214	90	107	218	120	0.318	95	218	240	0.98	98	216	180	0.76

[a] Based on rubber content after H_2S treatment.

TABLE III

EFFECT OF DIFFERENT AMOUNTS OF ZINC OXIDE, ZINC SULFIDE, AND SULFUR

(Temperature of vulcanization, 134° C)

Compound	Accelerator: Materials compared	Accelerator: % on rubber	Untreated: Max. modulus (Kg. per sq. cm.)	Untreated: Max. tensile (Kg. per sq. cm.)	Untreated: Vulcanization time (Min.)	H_2S-Treated: Max. modulus (Kg. per sq. cm.)	H_2S-Treated: Max. tensile (Kg. per sq. cm.)	H_2S-Treated: Vulcanization time (Min.)	Increase in wt. (%)
A[a]	Zinc oxide	4.0	179	295	120	66	101	120	1.65
	Sulfur	1.5							
B[a]	Zinc oxide	12.0	198	290	120	28	80	120	1.78
	Sulfur	1.5							
C[b]	Zinc oxide	12.0	239	285	120	53	123	120	1.70
	Sulfur	3.0							
D[b, c]	Zinc oxide	10.0	95	227	60	78	191	180	1.00
E[b]	Zinc sulfide	10.0	21	100	120	Not tested			

[a] Formula: rubber 100, carbon black 50, stearic acid 3, pine tar 2, benzothiazyl thiobenzoate 1.05, antioxidant 1.0, diphenylguanidine phthalate 0.70, zinc oxide and sulfur as shown; H_2S-treated 72 hours at 25° C.

[b] Formula: rubber 100.0, sulfur 3.0, stearic acid 0.5, mercaptobenzothiazole 0.75, zinc oxide and zinc sulfide as shown.

[c] H_2S-treated 15 hours at 25° C.

TABLE IV

EFFECT OF HYDROGEN SULFIDE ON THE RATE OF VULCANIZATION OF CARBON BLACK COMPOUNDS

(Formula: rubber 100.0, carbon black 50.0, zinc oxide 5.0, sulfur 3.0, stearic acid 3.0, pine tar 2.0, accelerator as shown; H_2S-treated 15 hours at 25° C; temperature of vulcanization, 134° C)

Accelerator		Untreated			H_2S-Treated			
		Max. modulus	Max. tensile	Vulcanization time	Max. modulus	Max. tensile	Vulcanization time	Increase in wt.
Name	% on rubber	(Kg. per sq. cm.)		(Min.)	(Kg. per sq. cm.)		(Min.)	(%)
Mercaptobenzothiazole	1.0	222	318	90	56	106	240	1.65
Diphenylguanidine + 2,4-dinitrophenylbenzothiazole	1.25	190	314	90	67	115	240	1.78

show that aldehydeamine accelerators and litharge react chemically with hydrogen sulfide, since in compounds containing these two materials absorption of the gas is greater, and part of it is retained permanently. Compounds containing carbon black also show a permanent absorption of part of the hydrogen sulfide. All compounds which indicate a permanent absorption of hydrogen sulfide (as shown by degassing in a vacuum) also indicate a retardation in the rate of cure and a permanent effect on the physical properties of the rubber compounds.

TABLE V

EFFECT OF HYDROGEN SULFIDE TREATMENT ON CHEMICAL AND PHYSICAL PROPERTIES OF RUBBER COMPOUNDS

(H_2S-treated 15 hours at 25° C)

Formula	J	K	L	M	N
Rubber	100	100	100	100	100
Zinc oxide	—	10	10	10	5
Carbon black	—	—	—	—	50
Sulfur	—	3	3	6.5	3
Pine tar	—	—	—	—	2
Stearic acid	—	0.5	0.5	—	3
Mercaptobenzothiazole	—	0.75	—	—	0.75
Litharge	—	—	—	10	—
Butyraldehydebutylideneaniline	—	—	0.5	—	—
% free S at max. modulus					
Untreated	—	0.425	0.395	—	0.60
Treated	—	0.59	0.560	—	1.10
% increase in wt. (based on rubber)					
After treatment	0.96	1.023	1.4	1.9	1.72
After degassing 2 hrs. at 5 mm.	0.05	0.05	0.4	0.9	0.76
Hours at room temp. to reach constant wt.	8	8	33	8	50
Max. modulus, kg. per sq. cm.					
Untreated	—	152	269	225	202
Treated and degassed	—	147	176	133	82

CONCLUSIONS

1. Rubber dissolves approximately one per cent of hydrogen sulfide when saturated at room temperature.

2. All types of commercial accelerators are retarded in rate of vulcanization as a result of treatment with hydrogen sulfide, and the retardation is directly proportional to the hydrogen sulfide content.

3. The physical properties of mercaptobenzothiazole types of accelerators and diphenylguanidine are not permanently affected by hydrogen sulfide, but dithiocarbamates, thiuram sulfides, aldehydeamines and litharge are permanently affected.

4. Rubber compounds containing mercaptobenzothiazole types of accelerators or diphenylguanidine, which have been treated with hydrogen sulfide and then degassed in a vacuum oven, show normal rate of vulcanization. Compounds containing aldehydeamines, litharge or carbon black show permanent retarding, even after degassing.

5. Increased zinc oxide or sulfur has no appreciable effect on the retardation.

6. Little or no zinc sulfide is formed as a result of treatment with hydrogen sulfide.

7. Hydrogen sulfide treatment of rubber compounds retards the rate of combination of sulfur with rubber.

8. In no case did hydrogen sulfide treatment improve the physical properties of the vulcanizate.

REFERENCES

[1] Am. Soc. Testing Materials, Rept. of Comm. D-11, Nov. 1939.
[2] Bedford and Gray, *Ind. Eng. Chem.* **15**, 720 (1923).
[3] Fisher, *Ind. Eng. Chem.*, **31**, 1386 (1939).
[4] Fisher and Schubert, *Ind. Eng. Chem.*, **28**, 211 (1936).

STUDIES OF HARD RUBBER REACTIONS VIII

THE CORRECTED COEFFICIENT OF VULCANIZATION, AND ITS UPPER LIMIT IN THE ACCELERATED RAW RUBBER COMPOUND *

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In a previous paper (*J. Soc. Chem. Ind. Japan* **40**, 111B (1939)) it was shown that compounds containing up to 60 per cent of sulfur give coefficients of vulcanization higher than the theoretical maximum value of 47. Strictly speaking, however, the sulfur present in these cases can be divided into the following parts: sulfur soluble in acetone; (a) true elementary sulfur; (b) sulfur combined with organic matter; sulfur insoluble in acetone; (c) sulfur combined with rubber; (d) sulfur combined with resins and proteins; (e) metallic sulfide.

In the present experiments, these five kinds of sulfur were separated as far as possible to determine the true or corrected coefficient of vulcanization, and its upper limit.

EXPERIMENTAL

The preparation of samples, etc., was carried out in a similar way as before (cf. Part I), except that the compounds containing 50 to 150 per cent sulfur on the rubber were as follow:

Mixings.....Raw rubber 100, zinc oxide 10, stearic acid 1, diphenylguanidine 2, sulfur 50 to 150 (50, 60, 70, 80, 90, 100, 150).
Cures.....5 to 300 minutes at 141° C.

The analytical procedure for the separation of true elementary sulfur from combined sulfur in the acetone extract and also for the determination of the acetone-insoluble sulfur, such as that combined with rubber resins, proteins or metallic zinc, was based on the method of Kelly (*Ind. Eng. Chem.*, **12**, 875 (1920)) which was somewhat modified by the author.

The sulfur combining with rubber was determined on the residual sample which had been extracted successively with acetone, alcoholic potash and ether-hydrochloric acid, as described in the above method, and the total percentage of combined sulfur was calculated for the original sample.

In an original sample, the percentage of pure rubber hydrocarbon which was necessary for determining the true coefficient of vulcanization was assumed to be 93.84 from the analytical data of the standard smoked sheet: acetone extract 3.2%, ash 0.23%, moisture 0.28% and protein 2.44% (*i.e.*, nitrogen 0.39% by Kjeldahl method).

If a considerable amount of hydrogen sulfide were evolved, and the amount of total sulfur were changed in the course of vulcanization, the values for the total sulfur content in the final products would not be identical with those of the mixes found before vulcanization. The corrected coefficient of vulcanization

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was therefore calculated from the data of the real total sulfur loss, of which $\frac{1}{16}$ was due to hydrogen in hydrogen sulfide, as shown in the following example:

Compound	Parts	%	Losses after 300 minutes' cure	%	Compound after 300 minutes' cure Parts	%
Rubber	100	51.45	$4.67 \times 1/16 = 0.29$ (calculated)		51.52	54.21
Sulfur	80	41.45	4.67 (found)		36.78	38.70
Other ingredients	13	6.74	0		6.74	7.09
Total	193	100.00	4.96		95.04	100.00

Coefficient of vulcanization

$$\frac{25.96 \times 100}{54.21 \times 0.9384} = 51.03$$

SUMMARY OF RESULTS

(1) As shown in Figures 1 and 2, the curves for acetone-soluble organic sulfide sulfur show rises and descents which may be attributed to polymerization or to depolymerization, due to some special sulfur compound formed during vulcanization. The second highest points in the curves, however, seem to bear

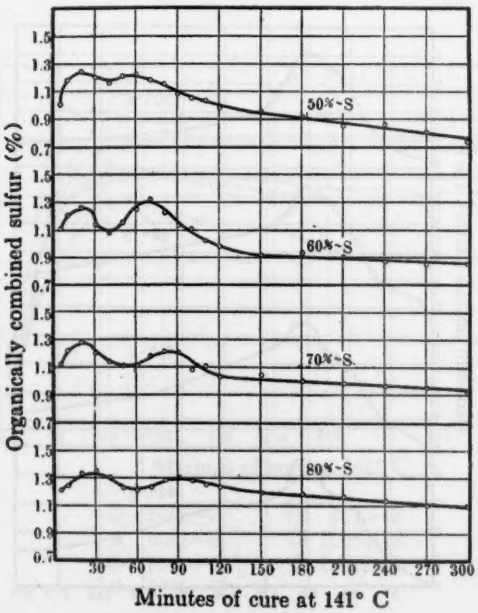

FIG. 1.

no relation to the time of the exothermic hard-rubber reaction of 90 minutes except for the mix containing 80% of sulfur. Generally, the formation of organic sulfide sulfur tends to increase with the increase in sulfur content of the original mix, and its marked change seems to be independent of each ingredient except sulfur, namely, accelerator, stearic acid, rubber resins, etc.

(2) It is evident from Figures 3 and 4 that for all compounds the time of the maximum production of sulfur in the alcoholic potash extract after acetone ex-

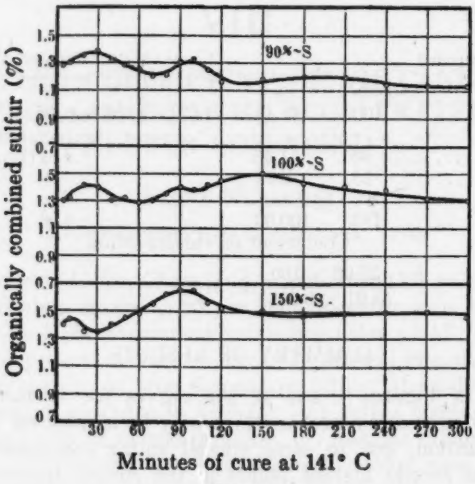

FIG. 2.

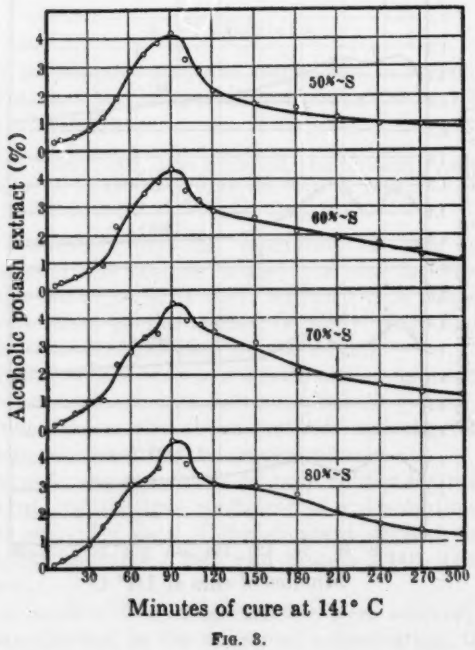

FIG. 3.

traction coincided with the cure time of 90 minutes which is the thermally active period in the hard rubber reaction. Considering this fact, the generation of alcoholic potash extract may be ascribed not merely to proteins or other

impurities in raw rubber, but to some extent to polymerization or depolymerization phenomena during vulcanization.

(3) The curves in Figure 5 show the sulfide sulfur formed from zinc oxide

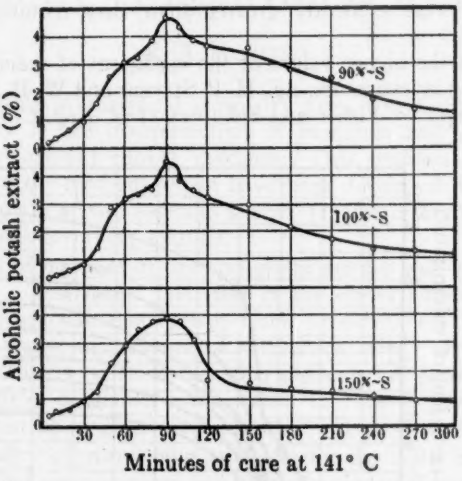

FIG. 4.

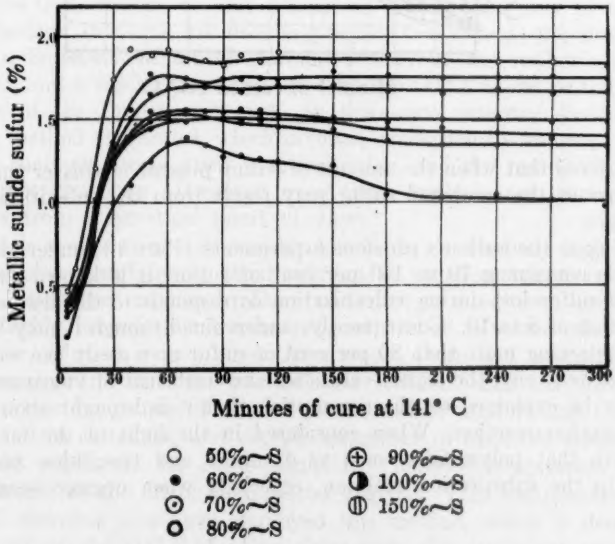

FIG. 5.

during vulcanization. In this case the parts of the curves corresponding to a lapse of about 50 minutes are generally of flat shape, and the reaction between sulfur and zinc oxide is considered to be a relatively simple chemical reaction which is hardly accompanied by polymerization or depolymerization of the rubber.

(4) As described above, the true or corrected coefficients were determined with the residual sample which had been removed from the other kind of sulfur combined with the non-rubber components. In cases of the compounds containing more than 80 per cent of sulfur, as shown in Figure 6, the true coefficients of vulcanization were evidently greater than that required for the formula C_5H_8S, *viz.*, 47.

The causes for the higher values of the coefficient of vulcanization have been discussed by other investigators, *e.g.*, H. P. Stevens and W. H. Stevens (*J. S. C. I.*, 1929, **48**, 55 T) and by Fisher and Schubert (*Ind. Eng. Chem.*, 1936, **26**, 209),

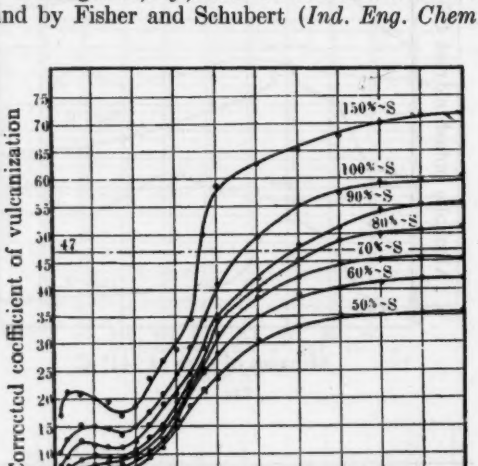

FIG. 6.

who considered that when the amount of sulfur present is greater than the theoretical, part of the combined sulfur may result from the substitution of sulfur for hydrogen.

According to the author's previous experiments (Part V), undertaken with the compounds containing 70 to 150 per cent of sulfur, it is known that the total amount of sulfur lost during vulcanization corresponds to the true coefficient of vulcanization of 8 to 10. Consequently, undervalued though it may be, the compounds containing more than 80 per cent of sulfur give easily the values exceeding 47, that is to say, the higher values for the coefficient of vulcanization cannot adequately be explained on the assumption that it is brought about merely by the substitution reaction. When considered in the light of the facts above, it would seem that polysulfides, such as disulfides and trisulfides, are formed in addition to the substitution reaction, especially when organic accelerators are present.

A NEW METHOD OF DETERMINATION OF FILLERS IN VULCANIZED RUBBER *

R. A. HUBLIN

One of the problems in analytical chemistry most frequently encountered in the rubber industry is the determination of inorganic and organic fillers in various types of vulcanized rubber products. This problem has been solved in various ways, and the methods which have been developed differ in efficiency and precision. They are of two essential kinds: (1) methods involving incineration, and (2) methods involving solution.

The shortcomings of methods of the first group are too well known to warrant any long discussion. Their chief fault lies in the errors which arise when the mixture to be analyzed contains carbon black or substances which oxidize or which decompose at the temperature of calcination, *e. g.*, carbonates, sulfides, hydroxides, etc. Naturally when incineration methods are employed merely for control tests of articles of known composition, they make it possible to work rapidly, and they can be of good service in this way.

But the impossibility of overcoming satisfactorily the faults mentioned above, without adding further complications, has led the majority of analysts to abandon incineration methods in favor of solution methods. It is possible, by means of a solvent which dissolves vulcanized rubber at a sufficiently low temperature, to separate fillers from rubber without damage of decomposing any of the fillers. Several methods of this kind are used in practice today, *e. g.*, the procedure of the American Society for Testing Materials[1], whereby the rubber is dissolved in mineral oil, and a similar procedure used by the O.C.E.M. to be found in the specifications of the French railways[2]. In this same category should also be included the method of Pontio[3], which involves extraction by cumene. The first two of these methods are of great practical value, and the results are accurate enough for most purposes. However, even these methods are inconvenient in various ways from a practical point of view.

Mineral oil is a solvent of vulcanized rubber only at relatively high temperatures, and to obtain sufficiently rapid solution in practice, temperatures of at least 150° C must be employed. Even under these conditions, especially in the case of highly loaded rubber mixtures and rubber mixtures containing reclaimed rubber, solution is very slow. As a result, there is a temptation to increase the temperature in order to accelerate solution. But this introduces a new and an important source of error, *i. e.*, the rubber mixture and the solvent themselves tend to carbonize, and deposit quantities of insoluble residue in the residual liquid which are far from negligible. These decomposition products vitiate the weight of the fillers obtained by analysis. This complication is well known to all chemists who have employed this method, which is described in Specification 47 of the O.C.E.M. Very frequently the analytical results show too high values, even when the procedure is followed scrupulously. However, when a rubber mixture of known composition is concerned, this can readily be taken into account in judging the results.

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* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Revue Générale du Caoutchouc* Vol. 17, No. 2, pages 49-50, February-March 1940.

The analyst is forced therefore either to accept analytical procedures which are rather tedious, or else to obtain results which are somewhat incorrect. Furthermore it is frequently very difficult to separate the fillers from the solvent. This is particularly true of mixtures containing carbon black, for in this case colloidal suspensions are formed, and the viscosity of the oil tends to increase the stability of these suspensions. Even after dilution, filtration is slow and often uncertain.

With a view to overcoming these faults, efforts were made to find a solvent with which it would be possible to carry out a determination fairly quickly and at a temperature low enough to avoid carbonization on the one hand and the difficulties of decantation and filtration on the other hand. At the very beginning a valuable clue was offered by a reference in an old work by C. O. Weber[4]. This author described a method of analysis by solution, whereby α-nitronaphthalene or nitrobenzene was used as solvent. The latter reagent was found to be particularly effective with rubber mixtures having low coefficients of vulcanization.

These two solvents were tested thoroughly by the present author. Insofar as rapidity of solution is concerned, the results were extremely promising, especially with α-nitronaphthalene. Even rubber mixtures containing high percentages of reclaimed rubber and carbon black, which can be dissolved in mineral oil only with difficulty, were completely dissolved in one-half to one hour at 160-170° C in α-nitronaphthalene. This in itself seemed to be a notable step forward. However, the actual manipulation involved certain inconveniences. For example, at ordinary temperatures, α-nitronaphthalene is solid, and after solution it recrystallizes in the receptacle. It is necessary therefore to dissolve it in a large excess of solvent, and when the liquid is then filtered, the edges of the filter become covered with crystals, which entrain solid particles and make it difficult to wash the residue thoroughly. In addition to this, carbonization still persists to a great extent because of the high temperature which is used, in spite of the short time required to effect solution. This can be readily demonstrated with rubber mixtures of known compositions.

Nevertheless, one step forward had been accomplished, in that a considerable saving in the time of operation was effected. The next problem was to determine whether this accelerated solution was due to the presence of the nitro group. To this end, the tests were repeated with pure naphthalene. It was found that solution in this hydrocarbon is much slower than in its nitro derivative. The presence of the nitro group is therefore of considerable advantage.

Memmler[5] has stated that anisol can be used as an agent for dissolving vulcanized rubber, with the advantage that it can be used at temperatures of 100° to 120° C. There is no doubt that this reagent can be used in this range of temperatures, but the times required are about the same as the times required with mineral oil at 150° C. In its favor is the fact that the danger of carbonization and of decomposition of the fillers, *e. g.*, antimony trisulfide, is practically eliminated. On the other hand, anisol is very expensive.

Recourse was then had to *o*-nitroanisol, with the hope that the presence of a nitro group, as in nitronaphthalene, would accelerate to a marked degree solution of the rubber. This supposition was found to be true by actual tests. The new reagent dissolved even the most refractory rubber mixtures in far shorter times (20 to 60 minutes) and at more moderate temperatures (100° to 120° C) than was found to be true with mineral oil.

In this way it was found possible to combine operation at a low temperature, to avoid any carbonization and decomposition of the fillers, with a procedure which could be carried through quickly. It was found also that *o*-nitroanisol has much less tendency to form colloidal suspensions of fillers than does mineral oil. Decantation can therefore usually be carried out very rapidly and completely.

Various types of liquids can be used as diluents, *e. g.*, benzene, toluene, petroleum ether, chlorinated compounds, etc. A mixture of equal parts of toluene and carbon tetrachloride is very effective. Toluene should be carefully rectified and should be absolutely free of heavy fractions. This diluent can be kept over anhydrous sodium sulfate.

The precision of the method just described was confirmed by careful tests of rubber mixtures of known compositions, containing a wide variety of fillers, including carbon black, various other blacks, whiting, zinc oxide, barytes, silica, slate, magnesium carbonate, kaolin, etc. In all cases, it was found that, with proper technique, values within 2 per cent of the correct ones were obtained. This precision is considerably better than that possible by the A.S.T.M. and O.C.E.M. methods, which very seldom give results within 5 per cent of the correct values, particularly when carbon black is present. In contrast to its behavior in the A.S.T.M. and O.C.E.M. methods, even reclaimed rubber does not prolong the time necessary for solution beyond reasonable limits.

The procedure which was finally adopted is the following.

PREPARATION OF THE SAMPLE BEFORE TREATMENT WITH THE SOLVENT

For preliminary treatment of the sample, reference should be made to the standard method of the American Society for Testing Materials[1], or to the specification of the O.C.E.M. of the French railways[2]. It is unnecessary to describe the procedures, for they appear in very complete form in these two specifications.

SOLUTION

After treatment in accordance with the specifications mentioned above, the sample, weighing approximately 1 gram, is finely divided, either by pulverizing or grinding on an experimental mill with the rolls very tight, or by cutting into very small pieces not over 1 mm. in size.

The sample is then placed in a conical flask of 100 cc. capacity, equipped with a reflux air condenser and a thermometer, together with 25 cc. of *o*-nitroanisol. The reservoir for the thermometer should be immersed completely in the liquid. A technical grade of *o*-nitroanisol is perfectly suitable, provided that it is first made certain that the *o*-nitroanisol contains no inorganic impurities or traces of acidity.

The flask is heated on an oil bath. Careful watch is kept of the rise in temperature, and the heating is regulated so that the thermometer indicates a uniform temperature of about 115° C during the process of solution. When the temperature of 115° C has been reached, it is maintained at this point for 30 minutes. In the great majority of cases, this length of time is sufficient for complete solution. If the rubber is still incompletely dissolved, the digestion is continued for perhaps 30 minutes more.

DECANTATION AND FILTRATION

After cooling, the contents of the flask is diluted with 150 cc. of a mixture of toluene and carbon tetrachloride, and is then allowed to stand until it can be decanted completely. This decantation can be carried out very rapidly when carbon black is absent, but requires several hours when carbon black is present in the rubber mixture.

The flask is covered with a watch glass. There is no difficulty in recognizing when to stop the decantation. A tared filter is then prepared with slow filtration paper (*e. g.*, Durieux Blue Ribbon). This filter paper should first be extracted thoroughly with carbon tetrachloride, or else special filter paper free of fats or oils should be used. The decanted liquid is filtered carefully, and the first part is filtered again until the filtrate no longer shows any turbidity. This filtrate is usually brown, and has the appearance of ordinary colloidal suspensions. A black color indicates that filtration is incomplete. When the supernatant liquid is completely filtered, the residue of fillers is added to the filter with the aid of a wash bottle containing the diluent. The fillers are washed thoroughly with the same hot diluent until all organic substances are completely eliminated. The tared filter paper containing the residue is then dried at 70° C and weighed.

APPLICATIONS OF THE METHOD

Not only is the new method applicable to the determination of fillers in rubber, but it is very well adapted also for determining the weight of rubber with which a fabric has been coated or impregnated. It is for instance easy to determine the rubber coating of an impermeable fabric or the weight of the rubber friction on a belt fabric.

Thanks to the low temperatures and the short times of treatment which are possible, cotton fabrics are affected very little by the process of dissolving away the rubber. Therefore it is possible, after extraction of the rubber, to test fabrics for their mechanical properties and to obtain results which are of some significance. In this case one would obviously not expect to be able to test specimens of fabric of normal size, but useful information can be obtained by cutting small strips, 1 cm. by 5 cm., and testing them. These small specimens can then be broken on a rubber dynamometer, with a speed of separation of 100 mm. per minute.

To be able to interpret correctly the results of these tests, it is advisable to make a corresponding series of tests of a fabric of similar construction and of known characteristics, and which also has been processed in the same way *i. e.*, frictioned or coated, then vulcanized, and finally the rubber removed by solution in *o*-nitroanisol under the conditions described. Instead of tensile measurements, small specimens in the form of discs can be subjected to bursting tests in an apparatus of the type used in the paper industry.

CONCLUSIONS

A new reagent, *o*-nitroanisol, makes it possible to determine the total filler content of vulcanized rubber much more rapidly and more precisely than heretofore. In addition, the procedure is easier than that of the classic method. It would therefore be desirable if the method of determining fillers by solution of the rubber, which can now be carried out so easily, were to be used in many

cases in place of incineration methods, which, in spite of being rapid, are very inaccurate, and also if the new method were to be used in place of the ordinary, relatively inconvenient solution methods.

REFERENCES

[1] Am. Soc. Testing Materials Standards, **1936**, Part II. Standard Methods of Chemical Analysis of Rubber Products, D 297-36, Rubber Solvent Method, pp. 1266-1267.
[2] O.C.E.M. des Chemins de Fer français. Analytical Part. Specification no. **47**.
[3] Pontio, "Analyse du Caoutchouc et de la Gutta-percha", Gauthier-Villars, Paris.
[4] Weber, "The Chemistry of India Rubber", Griffin, London, **1902**.
[5] Memmler, "Production et Traitements du Caoutchouc", Dunod, **1935**, p. 407.

SWELLING OF SYNTHETIC RUBBERS IN MINERAL OILS

EFFECT OF VARIATION IN ANILINE POINT OF OILS *

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Swelling of synthetic rubber compositions by mineral oils is of considerable interest to the rubber manufacturer and to the ultimate consumer of such products. Volume increase after immersion in an oil is often used as a criterion of the oil-resisting properties of a given stock, and is made an acceptance-test requirement of many purchase specifications. The purpose of this paper is to demonstrate the varying swelling effects of different mineral oils on Neoprene, Perbunan, and Thiokol compositions, and to suggest a new and practical method of specifying mineral oils to ensure duplication of performance.

Previous work by Fraser[2] showed that Neoprene vulcanizates, when immersed in lubricating oils, reach equilibria with respect to swelling and that the volume increase is a logarithmic function of the viscosity-gravity constant. The results of this study on Thiokol and Perbunan vulcanizates immersed in oil agree in general with the previous work on Neoprene, and further verify the varying effects of different commercial mineral oils purchased on the open market.

MATERIALS

COMPOSITIONS. Five synthetic rubber compounds were selected as representative of commercial stocks, and samples were immersed in ten mineral oils in this series of tests. These compositions were:

A Neoprene G compound, containing 70 volumes of soft carbon black (Thermax was used) per 100 volumes of Neoprene G. Extractable softeners were not used.

A Neoprene E compound, containing 185 volumes of fine cork per 100 volumes of Neoprene E.

A Perbunan Extra compound containing 53 volumes of carbon black and 9 volumes of extractable softener per 100 volumes of Perbunan.

A Perbunan compound containing 140 volumes of fine cork and 20 volumes of extractable softener per 100 volumes of the Perbunan.

A Thiokol DX composition containing a total of 125 volumes of carbon black and dust cork per 100 volumes of Thiokol.

All these compounds were prepared in sheet form by vulcanizing in a standard tensile sheet mold to the same extent as that used in commercial practice.

MINERAL OILS. Ten oils from various producers were purchased on the open market. The specific gravity, Furol viscosity at 100° F (37.8° C), and the aniline point were determined. The Furol viscosity was converted to Saybolt Universal by viscosity charts. The viscosity-gravity constant and the gravity index were calculated for each oil according to the methods of Hill and Coats[5] and of McCluer and Fenske[6]. Physical constants are shown in Table I.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 32, No. 8, pages 1069-1072, August 1940.

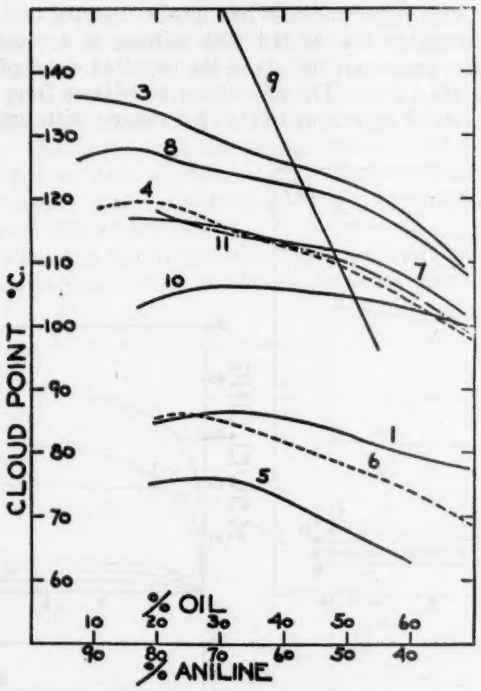

FIG. 1.—Cloud points of oil in aniline at various concentrations.

TABLE I

PHYSICAL CONSTANTS OF OILS

Oil no.[a]	Type of oil	Specific gravity (15.6° C)	Saybolt Universal viscosity (37.8° C) sec.	Viscosity-gravity constant	Gravity index	50% (by wt.) aniline point ° C
5	Plasticizing	0.9207	190	0.875	18	67.5
6	SAE 30 motor.....	0.9344	740	0.878	22	77.7
1	Plasticizing	0.8331	42	0.786	118	83.0
10	White oil	0.8813	215	0.822	95	104.8
9	SAE 30 motor.....	0.8709	540	0.794	115	107.0
11	SAE 30 motor.....	0.8836	600	0.810	105	109.5
7	SAE 30 motor.....	0.8831	590	0.809	106	110.8
4	SAE 30 motor.....	0.8833	480	0.813	105	109.0
8	SAE 30 motor.....	0.8708	530	0.794	116	119.8
3	High-viscosity paraffin	0.8937	2200	0.803	111	122.5

[a] Oil 2 in this series was cottonseed, which does not fall within the scope of this paper.

DETERMINATION OF ANILINE POINT

The method described by Gardner[4] was used with slight modifications because of the relatively high viscosities and the high aniline points encountered with mineral oils.

One gram of the mineral oil was weighed into a 15-mm. test tube; 0.25 cc. of freshly distilled aniline was then added from a 10-cc. buret graduated in

0.05-cc. divisions. This tube was inserted into a 25-mm. test tube containing glycerol, and the assembly was heated with stirring in a second glycerol bath until the temperature was about 10° above the expected cloud point. The oil and aniline solution was then clear. The tubes were withdrawn from the bath and allowed to cool at a rate of approximately 3° per minute with brisk stirring of the

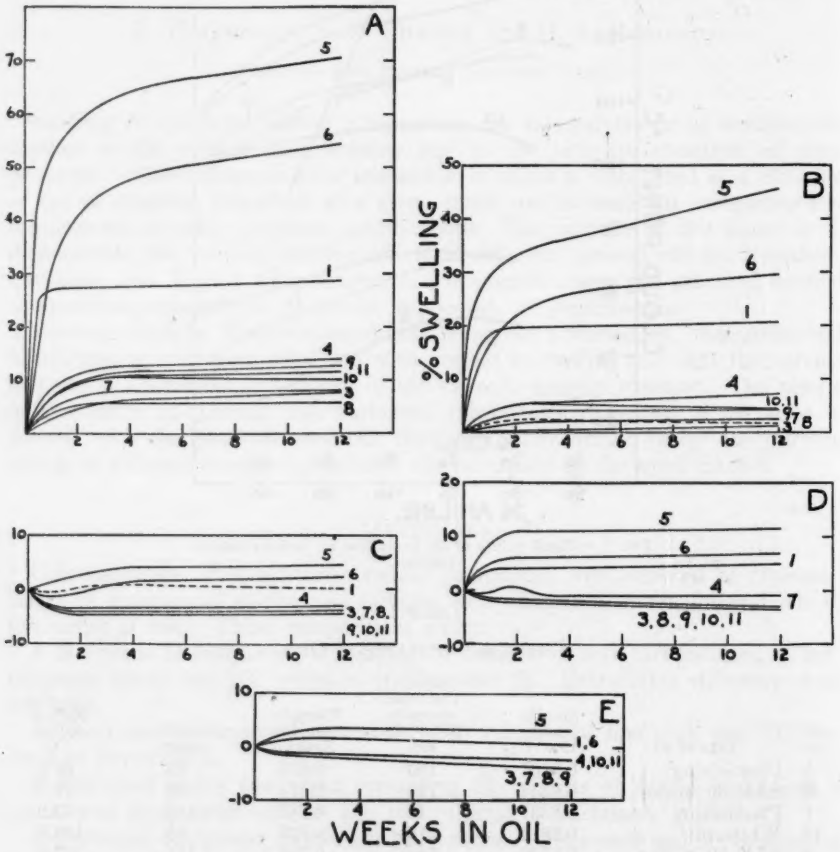

FIG. 2.—Swelling of compounds in oils of various aniline points.

A. Black-loaded Neoprene.
B. Cork-loaded Neoprene.
C. Black-loaded Perbunan.
D. Cork-loaded Perbunan.
E. Cork-loaded Thiokol.

solution. The aniline point for the mixture is that temperature at which the cloud first appears. Aniline was then added in 0.25- to 1.0-cc. portions, and the determination repeated until the cloud temperature on further addition of aniline did not increase.

The aniline point[4] is used as an index of the solvent power of volatile hydrocarbon solvents, the higher aniline point indicating less solvent power. The maximum cloud temperature is normally taken as the aniline point. In the case of volatile solvents, this point is found at about 50 per cent aniline; but with

mineral oils it occurs at progressively higher concentrations of aniline as the viscosity, and therefore the molecular weight, of the oil increases (Figure 1).

Fuchs and Anderson[3] examined mineral oils from various fields, which were extracted to the same aromatic content. They found that the aniline point decreases in the following order: Pennsylvania, mid-continent, West Texas, and Gulf Coast fields. They show that the aniline points of their SAE 40 oils vary from 115 to 94, whereas those of their SAE 20 oils vary from 102 to 86. These aniline points are higher than for nonextracted oils, since the refining operation removes materials of high solvent power.

Previous experience has shown that the 50 per cent aniline point is a less reliable index of the solvent action of the oil than the maximum cloud or the

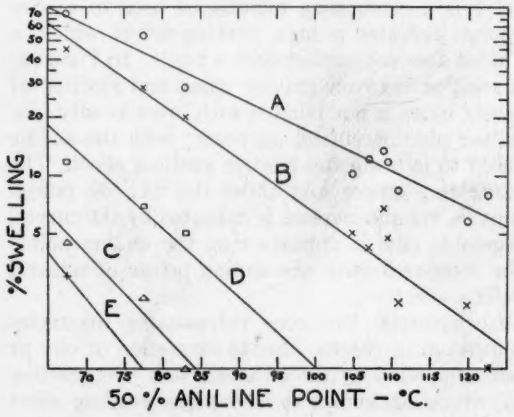

FIG. 3.—Aniline point of oil *vs.* logarithm of per cent swelling.

A. Black-loaded Neoprene.
B. Cork-loaded Neoprene.
C. Black-loaded Perbunan.
D. Cork-loaded Perbunan.
E. Cork-loaded Thiokol.

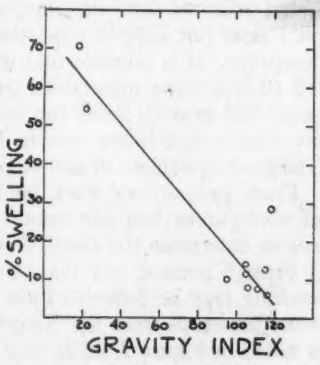

FIG. 4.—Swelling of black-loaded Neoprene as a function of the gravity index.

critical solution temperature. However, since the 50 per cent aniline point (by weight) requires but one determination and is more widely employed in the oil industry, it was selected as a basis for comparison in this study.

Examination of the curves in Figure 1 shows that oil 9 has a much steeper slope than any of the other oils examined. This oil contains a small amount of polyolefin, the presence of which is responsible for this behavior. In this case "haze" points rather than true cloud points are observed, as two-layer separation does not occur. It is believed that oils containing polyolefins may be recognized by this behavior. Further work is in progress to develop methods for determining the true aniline point of such oils.

TEST PROCEDURE. Samples of each stock, $1\times2\times0.1$ inch ($2.5\times5\times0.25$ cm.), were placed in the different oils, and percentage volume increases were determined after 1, 2, 3, 4, 6, and 12 weeks of immersion in small individual stoppered bottles held in a constant-temperature cabinet at $70°\pm1°$ C. Volume changes were determined by the displacement method, according to the procedure of the American Society for Testing Materials[1].

SWELLING RESULTS

The time-swelling curves for each compound in the different oils are shown in Figure 2. Figure 3 gives aniline point *vs.* the logarithm of the percentage volume change of the various compounds; the data for the low-swelling materials extend into the next lower decade and actually permit a curve to be drawn. These points are not represented here, but may be obtained by averaging the 6-12 week swelling points from Figure 2, *C*, *D*, and *E*.

From Figure 2 it is evident that oil 5 causes the greatest swelling of all stocks, and has the lowest aniline point. This oil is a type generally used for plasticizing natural or synthetic rubber; the excellent softening properties are indicated by the swelling tests and the low aniline point. Oil 6 is a well-known SAE 30 lubricating oil; both the gravity index and aniline point indicate the high swelling effect, which is shown in all curves. Oil 1 is a plasticizing mineral oil used in rubber compounding, and the aniline point indicates a high swelling effect which is found in actual test; the gravity index does not predict such a result. In Figure 4, oil 1 does not show a consistent relation between gravity index and swelling of Neoprene. It is possible that gravity index is not reliable with low-viscosity oils. Oil 10 is a white mineral oil used for pharmaceutical purposes; both the aniline point and gravity index can be used to indicate the relative swelling effect. The six remaining oils are various lubricating grades sold under the SAE 30 rating. The good agreement of aniline point *vs.* volume increase is indicated by the curves.

From preliminary work on vegetable oils, it appears that the aniline points of nonhydrocarbon oils cannot be compared with the aniline points of mineral oils to determine the relative swelling effect.

Fraser[2] pointed out that, with commercial Neoprene vulcanizates, maximum swelling may be followed by a shrinkage in volume, due to extraction of oily or waxy materials from the Neoprene compound by the oil under test. Contraction is noted in Figure 2, *C*, *D*, and *E*, where oils known to have a low swelling effect have actually caused a shrinkage in volume. This is particularly true of those synthetics which are least affected by oil and which contain extractable material.

CONCLUSIONS

1. There is a marked difference in the swelling caused by different mineral oils on compounds made of any synthetic rubber, such as Neoprene, Thiokol, or Perbunan; the arrangement of the oils by swelling effect tends to remain the same for the synthetic compounds tested.
2. The change in volume is rapid on initial immersion and then gradually approaches equilibrium, except in the case of those systems where marked swelling is encountered.
3. The aniline point, determined at a concentration of equal parts of aniline and oil by weight, appears to be a characteristic of mineral oil which will indicate the probable swelling effect on synthetic rubber compounds. The 50 per cent aniline point is more conveniently determined than is the gravity index, and appears to be at least equally reliable.
4. The viscosity rating of a mineral oil is not a satisfactory criterion of its tendency to swell rubberlike compositions, and should not be the sole description of an oil for acceptance specification testing of synthetic rubber products.

ACKNOWLEDGMENT

The authors wish to thank F. M. Gavan for obtaining many of the data and charting them.

REFERENCES

[1] Am. Soc. Testing Materials Standards Year Book, Pt. 3, p. 837, Designation D471-37T (1939).
[2] Fraser, *Ind. Eng. Chem.* **32**, 320 (1940).
[3] Fuchs and Anderson, *Ind. Eng. Chem.* **29**, 319 (1937).
[4] Gardner and Sward, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors", 9th ed., Inst. of Paint and Varnish Research, Washington, D. C., 1939, p. 417.
[5] Hill and Coats, *Ind. Eng. Chem.* **20**, 641 (1928).
[6] McCluer and Fenske, *Ind. Eng. Chem.* **24**, 1371 (1932).

COLOR REACTIONS BETWEEN CLAYS AND AMINES *

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A study of the discolorization of white side-wall tires has led to the discovery of brilliant color reactions between a number of organic compounds used as antioxidants in the rubber industry and different clay minerals[1]. This paper concerns itself with a more detailed study of this phenomenon[2].

Since it was found that all the rubber antioxidants which gave color reactions with the clays were amines, it was first desirable to ascertain whether the reaction is dependent on the presence of nitrogen as such, or whether an amino group is essential. Furthermore, it seemed of importance to determine whether the reaction occurs with aliphatic as well as aromatic amines. Finally, it was considered of value to establish as many methods of bringing the reaction about as possible.

The original experiments using clay and rubber antioxidant were limited to the formation of the color by allowing the dry clay and dry antioxidant to react with each other. The reaction, caused by direct contact or due to the vapor pressure of the antioxidant at room temperature, was slow and in the latter case confined to the exposed surface of the clay.

Since then it has been ascertained that the color—all shades of the spectrum have been produced—can be developed by either grinding the dry components together in a mortar or by mixing the clay with the reactant in the presence of a few drops of water. If the reactants are liquids, the color will appear immediately on contact with the clay. In the case where water-soluble salts of the reactants are available, the color will appear immediately if the clay is added to the aqueous solution. Special care was taken to purify all chemical reagents as highly as possible.

We have listed in Table I a great number of compounds, together with the color they form in combination with Wyoming bentonite (Al-Si-montmorillonite), both in basic and acid condition. All basic reactions were performed by mixing the liquid amines with the clay, by adding a few drops of water to the dry mixture, or by mixing the dry amine into clay hydrogel. In the acidic range a hydrogel of an acidified clay was used, to which either the liquid or solid amine was added.

A detailed survey of Table I reveals the following facts: Only certain amines (1) of the aniline type give the color reaction. Similar aromatic compounds with nitrogen attached to the benzene nucleus give various colors, depending on the type of substituents present (70, 71, 72; 21, 22; 51, 52; 61, 62, 63; 27[3], 32, 68). Aliphatic amines (3, 44, 76) as well as saturated cyclic amines (31) give no reaction. Nitrobenzene (50) and heterocyclic nitrogen compounds (64, 66) and compounds with the amino groups removed from the benzene ring (30) are nonreactive. An acetyl group on the nitrogen inhibits color formation (1, 28, 36, 53, 54, 55, 56, 73, 74, 75). Alkyl groups substituted in the amino group intensify

* Reprinted from the *Journal of the American Chemical Society*, Vol. 62, No. 7, pages 1811-1814, July 1940.

TABLE I

No.	Compound	Basic color	Acidic color
1	Acetanilide	—	—
2	Acetophenone, *p*-amino-	Green	Yellow
3	Ammonia	—	—
4	Aniline	Green	—
5	Aniline, *p*-aminodimethyl-	Blue	Pink
6	Aniline, *p*-aminodiethyl-	Tan	Green-blue
7	Aniline, *p*-bromodimethyl-	Green	—
8	Aniline, diethyl-	Green	—
9	Aniline, dimethyl-	Green	—
10	Aniline, ethyl-	Green	—
11	Aniline, methyl-	Green	—
12	Aniline, *m*-nitro-	—	—
13	Aniline, *p*-nitro-	Green	—
14	Aniline, 4-nitro-2-chloro-	Green	—
15	Aniline, *o*-nitrodimethyl-	Orange	—
16	Aniline, *p*-nitrodimethyl-	Yellow	—
17	Aniline, *m*-nitromethyl-	Yellow	—
18	Aniline, *p*-nitromethyl-	Yellow	—
19	Aniline, *p*-nitrosodimethyl-	Brown	Yellow
20	Aniline, tribromo-	—	—
21	Anisidine, -*o*-	Pink	Blue
22	Anisidine, -*p*-	Purple	Blue
23	Anthranilic acid	—	Pink
24	Anthraquinone, 1-amino-(red)	No change	
25	Anthraquinone, 2-amino-(red)	No change	
26	Benzene, *p*-aminoazo-	Brown	Pink
27	Benzidine	Blue	Yellow
28	Benzoic acid, acetyl-*o*-amino-	—	—
29	Benzoic acid, *p*-amino-	—	Yellow
30	Benzylamine	—	—
31	Cyclohexylamine	—	—
32	Dianisidine-*o*	Green	Pink
33	Diphenyl, *o*-amino-	—	—
34	Diphenyl, *p*-amino-	Weak green	—
35	Diphenylamine	Blue	Blue
36	Diphenylamine, acetyl-	—	—
37	Diphenylamine, 4-amino-	Yellow	Blue
38	Diphenylamine, isopropoxy-	Green	—
39	Diphenylmethane, *p*-diamino-	Pink	—
40	Diphenylmethane, tetramethyl-*p*-diamino-	Gray	—
41	Hydroquinone	—	—
42	Metanilic acid	—	Pink
43	Michler ketone (tetramethyl-diaminobenzophenone)	Green	Yellow
44	Monoethanolamine	—	—
45	Naphthylamine, α-	Green	—
46	Naphthylamine, β-	Pink	—
47	Naphthylamine, di-β-	—	—
48	Naphthyl, di-β-*p*-phenylenediamine	Pink	—
49	Naphthylamine-1 Trisulfonic acid-3,6,8	—	—
50	Nitrobenzene	—	—
51	Phenetidine, *o*-	Pink	Blue
52	Phenetidine, *p*-	Purple	Blue
53	Phenetidine, *p*-acetyl-	—	—
54	Phenol, acetyl-*m*-amino-	—	—
55	Phenol, acetyl-*o*-amino-	—	—
56	Phenol, acetyl-*p*-amino-	—	—
57	Phenol, *p*-amino-	—	—
58	Phenylethylmethanolamine	Green	—
59	Phenylmethanolamine	Green	—
60	Phenyl-β-naphthylamine	Pinkish green	—
61	Phenylene-*m*-diamine	Green	—
62	Phenylene-*o*-diamine	Yellow	Pink

TABLE I—*Continued*

No.	Compound	Basic color	Acidic color
63	Phenylene-*p*-diamine	Purple	Pink
64	Pyridine	—	—
65	Quinone	—	—
66	Resin "D"	—	—
67	Sulfanilic acid	—	—
68	Tolidine, *o*-	Blue-green	Yellow
69	*p*-Toluenesulfonylmethylaniline	—	—
70	Toluidine, *m*-	Yellow	Orange
71	Toluidine, *o*-	Yellow	Orange
72	Toluidine, *p*-	Pink	—
73	Toluidine, *m*-acetyl-	—	—
74	Toluidine, *o*-acetyl-	—	—
75	Toluidine, *p*-acetyl-	—	—
76	Triethylamine	—	—
77	Triphenylamine	—	—

the color (8, 9, 10, 11). Aryl groups exhibit a similar effect (35, 37, 38, 60). NH_2 as a ring substituent intensifies the color (61, 62, 63; 5, 6, 8, 9). NO_2, SO_3H, COOH, R, OR, acetyl, Br, and OH reduce or inhibit color formation (7, 12, 13, 16, 17, 18, 20, 23, 29, 33, 34, 39, 40, 42, 45, 46, 49, 57, 67, 70, 71, 72). The position of methoxy and ethoxy groups is important. In ortho position (21, 51) they lighten the color; in para position (22, 52) they deepen it. Compounds of the benzidine type (27, 32, 68) and the naphthylamines (45, 46, 47, 48, 49, 60) give deep colors. The color will be the lighter the more acidic the ring substituent.

The color is specific to the amine and can be produced with all reactive types of clay (bentonite, fullers' earth, kaolin, zeogel, etc.).

The benzidines give blue, anilines green, and toluidines pink or yellow colors.

The intensity of the color depends on the type of clay. Zeogel, bentonite, fullers' earth, kaolin, etc., form colors of decreasing intensity in the order given. China clays and illites react only slightly. Powdered silica, silica aerogel, aluminum oxide, ground mica and ignited bentonite are nonreactive.

The fact that Wyoming bentonite thus colored will still swell in water and permit base-exchange suggests that the color reaction is not to be regarded as a simple base exchange phenomenon. The addition of excess amines results in making the color dull or even black. By either adding more clay or simply washing the excess amine off, the brilliancy of the color reappears immediately. To test the possibility that the color might be due to a reaction between the amine and oxygen, or an oxidizing agent adsorbed or entrapped in the clay structure, the experiments were repeated with carefully prepared oxygen-free pure clay. No change in character or intensity of the colors could be observed.

It is interesting to note that where the color is obtained by mixing clay and solid amine in the presence of water, the products return to their original colorless state on drying. However, the color can be restored on wetting.

In certain cases the change in color on drying is a process involving progressive lightening of color. *o*-Tolidine dries from blue to green to yellow to colorless, as do benzidine and *o*-dianisidine. The compounds containing only one aromatic ring dry out directly to the colorless state. The color changes from the wet to dry state are the same as those obtained by adding acid to the colored clay. The liquid amines apparently hold their color even when dry, and the colors produced by grinding dry clay and solid amine also persist without added moisture. In cases where clay is added to the amine hydrochloride, the acid apparently base

exchanges with the clay. The amine, no longer solubilized, then contacts the clay surface. There is no evidence that the color can exist independently of the clay. Whenever a suspension of the colored clay is made in any liquid, the color settles with the clay, leaving a clear supernatant liquid.

It has not been possible to remove any of these colors from the clay and maintain them in solution or in the solid state. Attempted extraction[4] of the green color of dimethylaniline with acetone gave a colorless wash liquid which proved to be acetone and unreacted amine. The clay was colorless and found to be unaltered in its properties. Similarly, benzidine and clay were recovered from their blue reaction product.

Dimethylaniline is a notable example of the color reactions, in that it gives first a green color and then, either after standing or on heating, a blue color and finally a purple color[5]. The last shade is different in character from those previously mentioned, it being no longer reversible and definitely associated with the clay. It exists as well in the dry state as in the moist and is unaffected by mild heating. It cannot be removed by solvent extraction, but if it is treated with acid the purple clay turns to a dark green in color; when washed with acetone or dioxane, the wash liquor is purple, although the clay remains green. Water washing of either the purple or green clay produces no detectable change in the clay or in the wash liquor. This purple clay has lost its ability to swell in water and no longer forms colloidal suspensions in water.

If environmental conditions are changed, the reaction is thereby noticeably affected, revealing the following noteworthy trends.

Mineral and organic acids either inhibit or lighten the color. For example, *o*-tolidine (68) shifts from blue to yellow, aniline from green to colorless[4], *p*-aminodimethylaniline[5] from blue to pink. Bases added to the colored clay in neutral media have no effect, but when added to the acidified clays restore the original basic color. Thus, benzidine (27) can be shifted from blue to yellow and back to blue any number of times by additions of acid and base, respectively. Reducing agents, such as stannous chloride and formaldehyde, reduce the color or destroy it completely, just as do the acids. If one adds an oxidizing agent to such a mixture, the color is restored. Potassium chlorate will restore the pink color to acidic *p*-aminodimethylaniline (5) which has been reduced to the colorless state with stannous chloride. If one adds either the acid or reducing agent to the clay before the amine is introduced, the lighter or colorless state is immediately obtained, and can be shifted to the darker shade by suitable addition of a base or an oxidizer. The presence of solvents for the amines reduces the amount of color; the deficiency is proportional to the solubility of the amine in the solvent and to the amount of solvent present.

It is today generally assumed that the appearance of color in a compound results from a special type of resonance, and the depth of the shade is considered a measure for this phenomenon. With the type of compounds which have been shown to give the brilliant clay colors, one can easily visualize the provocation of resonance.

In the case of the amines and the clay, it has been shown that no reaction products are attainable for analysis, but that the original reactants return on separation. Therefore, one cannot ascribe the color to any addition to the nitrogen atom. However, that this atom is responsible for the reaction is indicated by the activity of compounds with ring substituents in all possible positions, particularly by the para-substituted dialkylanilines. Moreover, the action of excess

acid in inhibiting color formation and the return of the color in basic solution suggest that nitrogen in the lower state of valency is the active factor.

The most probable cause of color formation in compounds of this type would be oxidation. Atmospheric oxygen colors most of the compounds used. However, it does not give the shades found on clay. The color formation with clay is favored by alkaline media and inhibited or lessened by acids. Moreover, the presence of acidic substitutents in the molecule lessens the tendency to form color, while basic substituents promote deeper shades. Reducing agents inhibit the reaction. Oxidizing agents favor it. All these facts suggest that oxidation is the actual cause for the appearance of color.

The possibility that adsorbed or occluded oxygen or an oxidizing agent is responsible for the reaction already has been eliminated. However, the surface of a clay particle has many points of unsaturation where metallic atoms have unsatisfied residual valences, created when the clay crystal is ruptured. These metallic atoms are part of the lattice structure of the clay and therefore cannot be removed.

The metallic atoms involved will be those which occur in the unsubstituted crystalline structure, as the substituted metals of lower valence are already saturated and create the excess negative charges as the clay particle to which base-exchange is attributed.

The reaction might be explained as follows. The amine, after it is brought into close contact with the clay particle, is adsorbed by the available unsaturated metal groups on the surface. One of the unshared electrons in the nitrogen outer shell is transferred into the crystal structure, setting up on unbalanced force field in the amine. This condition provokes resonance in the amine, and the quinoidal structure is obtained. In this way the amine acts in a similar manner to what would be the expected action of a reducing agent and it is easily seen why reducing agents inhibit the reaction, *i.e.*, the reducers having more readily transferred electrons act as donors rather than the amine. Similarly, this reaction could occur with aliphatic and heterocyclic amines, without formation of colored compounds, and the aromatic amines added after these others would not react.

As long as the aromatic nitrogen atom and the unsaturated metallic atom are in close contact, color will persist. On separation the nitrogen becomes stabilized and the clay is restored to its original state. Nitrogen with all electrons shared, such as in nitrobenzene and the amine salts (if their salt acid is not removed), will not be capable of undergoing this reaction.

It is probable that some association between resonating molecules will occur in the close-packed adsorbed layer on the surface of the clay. This would tend to give deeper colors and account for the greens in the benzene derivatives, where ordinarily imine molecules would be yellow. This association would not be permanent, and one would expect to be able to regain unreacted amines, as actually is the case. If the compound were highly reactive, however, one might expect a coupling by some means between the molecules, and this would explain the formation of the purple clay from the green dimethylaniline product.

In the case of the compounds which exhibit different colors in acidic and basic media, the extent of the resonance will be the controlling factor in color. Benzidine in basic media gives a deep blue color, in acid a yellow color and in highly acid solutions no color at all. Preliminary tests seem to indicate that the color is determined by the amount of acid salt formed with the amino groups. Thus, in basic media no salt formation occurs, and the resonance goes through

the two rings of the biphenyl nucleus, resulting in a deep blue. If sufficient acid is added to form salt with one-half the amine present, the resonance is restricted to one ring and, since association is prevented spatially, the yellow color typical of imine compounds is produced. More acid forms salt with all of the amino groups, no resonance is induced, and a colorless state results.

The experimental data and the hypothesis as offered point toward various possibilities to stabilize the colors obtained. Work in this direction is being continued, as well as a more detailed study of the actual mechanism of the color reaction. It is hoped that these results can be presented in the very near future.

SUMMARY

The formation of colored compounds on clay has been shown to be the result of a reaction between clay and aromatic amines.

The influence of various substituents, acid and bases, is discussed.

A preliminary hypothesis explaining the mechanism of the reaction is advanced and further work outlined.

REFERENCES

[1] A brief report of the earlier observations, made jointly with T. J. Cater, Jr., was presented by one of us (E.A.H.) before the Division of Colloid Chemistry at the meeting of the American Chemical Society in Boston, September 11-16, 1939.

[2] This paper is largely a condensed review of the M.S. thesis of M. B. Leggett.

[3] G. Stern of the U. S. Bureau of Mines informed us during the course of this work that he had observed a strong color reaction between benzidine and bentonite in the presence of water.

[4] All extractions were done in the cold to prevent formation of the usual amine oxidation products.

[5] After presentation of this paper, there appeared in *Chemical Abstracts* **34**, 1976 [8] (Apr. 10, 1940) an abstract of a paper by Eisenack in the *Zentr. Mineral. Geol.* **1938**, [A], No. 10, 305-8, outlining preliminary observations on reactions similar to this one. The author found essentially the same phenomenon as this further reaction of dimethylaniline, using several aromatic amines.

BUNA IN THE MANUFACTURE OF CABLES *

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INTRODUCTION

The production on an increasingly large industrial scale of the synthetic rubberlike material, Buna, has led to its steadily expanding use in all branches of industry. The cable industry in particular has become interested in the properties of the various types of Buna in a large way in some of its extensive development problems. Buna S and Buna SS (formerly Levulkan), which have excellent aging, heat-resistant and insulating properties, are for example being used for insulating the metallic conductors of the various types of cables and cords for heavy current and low current service.

Vulcanized Buna S as well as vulcanized Perbunan (formerly Buna N), the latter having the character of a semiconductor, are being used for the protective jackets of portable cables, ship cables, mine cables and telephone cables. Cable coverings made with Buna are characterized by their high stability over a wide range of temperatures, and by their great resistance to mechanical forces, which is manifest for example in a resistance to abrasion greater than that of natural rubber. In addition, Perbunan has much greater resistance to oils, fats and benzine than does natural rubber.

Not only does cable manufacture require a material with high insulating properties and a cable covering of high mechanical quality, but also it is desirable that Buna, if used, have properties which make it process satisfactorily. Most Buna mixtures designed for insulation can be processed in strip-covering machines, Buna mixtures for coverings in ordinary extrusion machines.

An extensive experimental program has been necessary to find a way of meeting all these frequently conflicting requirements with a new raw material like Buna. It seems advisable, therefore, to describe in a brief way the electrical and mechanical properties which can be obtained in cable manufacture with Buna as a result of these prolonged experiments.

INSULATION RESISTANCE

Among the various electrical properties of Buna mixtures, specific resistance, loss angle, and dielectric constant give the best idea of the mixtures as insulating materials. It is interesting, by means of these electrical constants, to follow Buna through the various processes of manufacture from the raw material to the finished cable, and thus to be in a position to solve, by physical measurements, the numerous technical problems which arise in the factory.

In investigations of this kind, natural rubber can always be included, and thereby compared with Buna, particularly since Buna is now a perfectly satisfactory substitute for natural rubber, in fact is superior in many respects.

First of all, let us consider specific resistance, which is a measure of the insulating value of a raw material. Since it is desirable that the specific re-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk*, Vol. 16, No. 3, pages 26-33, March 1940.

sistance remain constant over the widest possible range of temperatures, determinations were first made of the specific resistances of natural rubber and of the various types of Buna, when uncompounded and unvulcanized, as a function of the temperature (see Figure 1).

If the specific resistances of the various raw materials at 20° C are first of all compared, it will be seen that Buna S, Buna SS and natural rubber are all suitable technical materials for insulation. Buna S, with a specific resistance of 10^{14} ohms per cm., does not reach the specific resistance of natural rubber, with values of 5×10^{15} to 10^{16} ohms per cm. Buna SS, with a specific resistance of 5×10^{14} ohms per cm., approaches more nearly to that of natural rubber. Quite distinct from this group of insulating materials, Perbunan has a specific resistance of only 5×10^{10} ohms per cm.

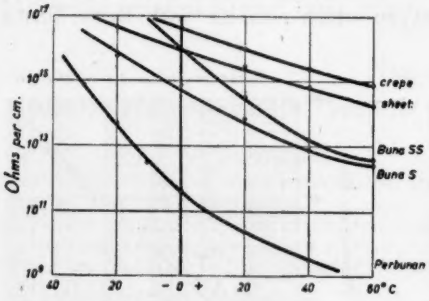

FIG. 1.—Specific resistance of rubber and Buna as a function of temperature.

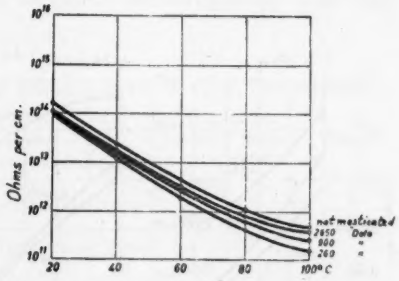

FIG. 2.—Influence of the plasticity on the specific resistance of raw Buna S at various temperatures.

TABLE I

Type of rubber	Specific resistance (ohms per cm.) 20° C	0° C	Temperature coefficient of the specific resistance between 0° and 20° C = 20α
Crepe	1×10^{16}	7×10^{16}	−0.85
Sheet	3×10^{15}	1×10^{16}	−0.70
Buna SS	5×10^{14}	1×10^{16}	−0.95
Buna S	1×10^{14}	8×10^{14}	−0.87
Perbunan	3×10^{10}	5×10^{11}	−0.94

The values of the specific resistance recorded in Figure 1 were obtained with a mirror galvanometer, with a direct-current voltage of 1000, and with measurements 1 minute after application of the voltage.

Since in cables carrying currents, the insulating layer becomes heated as a result of electric losses, it is important to know its insulation resistance at elevated temperatures as well as at ordinary temperatures. As is evident in Figure 1, the specific resistances of all types of rubber diminish with increase in temperature. Table I shows the decreases in specific resistance between 0° and 20° of the various types of rubber, *i. e.*, the temperature coefficients (in these cases negative) of these materials, based on a temperature differential of 20° C. The decreases in specific resistance with increase in temperature are greater for all types of uncompounded, unvulcanized Buna than for natural rubber.

The relation between specific resistance and temperature is such that the insulating properties of the various types of rubber are better when cold than

at ordinary temperature. Thus the higher temperature coefficient of Buna SS is of such a magnitude that its specific resistance at 0° C exceeds that of natural rubber. Even the semiconductor Perbunan becomes an insulator at −15° C.

Instead of following the conventional method of plasticizing natural rubber by mastication on roll mills, Buna S and Buna SS are today frequently plasticized by the more economical method of softening by heat treatment. This process is particularly important in that it offers the possibility, in the manufacture of rubberized conductors on strip covering machines, of obtaining uniformly perfect joints. In this connection the question arises whether the specific resistance is affected by the thermal treatment of the Buna.

The plasticities of samples of Buna S which had been softened by heat treatment to different stages of plasticity were measured by the same method and in the same units used for rubber. The results are shown in Figure 2. It is evident that the appreciable traces of oxygen which combine with Buna during

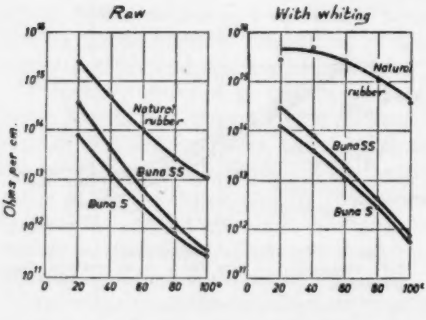

FIG. 3.—Influence of loading on the specific resistance at various temperatures. (Mixture: Buna 100, sulfur 1.2, accelerator AZ 0.8, stearic acid 1, zinc oxide 2, whiting 200.)

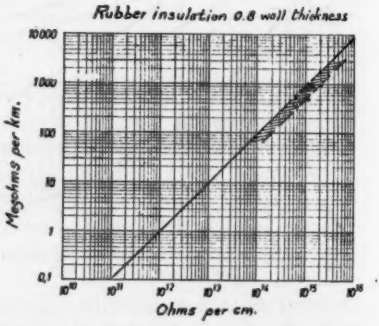

FIG. 4.—Relation between the specific resistance of sheets and the insulation resistance of conductors.

the thermal softening process do not change to any marked degree either the specific resistance itself or the temperature coefficient of this specific resistance.

The next step after plasticizing, in the processing of rubber mixtures for insulation, is the mixing of fillers, softeners, sulfur and accelerators into the plasticized raw rubber. This process too was followed with the aid of a temperature-specific resistance diagram.

The influence of fillers at a definite degree of vulcanization was first studied. In this series of measurements, whiting was chosen as filler. Figure 3 shows the changes in specific resistance as a function of temperature, both for the raw mixtures and for the same mixtures after vulcanization. In this case the mixtures contained 200 parts of whiting per 100 parts of Buna or natural rubber. The left-hand diagram of Figure 3 shows the results obtained with the raw rubbers; the diagram on the right shows the data for the compounded, vulcanized rubbers, including natural rubber, Buna S and Buna SS. In this case, neither Buna S nor Buna SS was softened by heat treatment. In all three cases, loading with a filler and vulcanizing had a favorable effect on the temperature coefficients; furthermore, notwithstanding the flattening of the temperature-specific resistance curves, the relative values of the temperature coefficients remained unchanged, *i. e.*, loading with whiting and subsequent vulcanization did not have any effect on the relative values. Again Buna SS had the highest temperature coefficient, followed in order by Buna S and natural rubber.

PROPERTIES OF COVERED CABLES

After this comparison, the next step was to test a series of technical mixings, containing various fillers and softeners, which had been vulcanized and which, in the case of Buna, had been prepared from thermally softened raw material. The sample sheets were vulcanized in steam in accordance with the factory process of vulcanizing conductors, and were first tested without drying (see Table II).

At the same time an attempt was made to find a relation between the insulation resistances of strip-covered conductors and the specific resistances of sample sheets of insulating mixtures out of which the conductors were made. The mixtures selected contained 33 per cent by weight (about 55 per cent by volume) of rubber. Talc, precipitated whiting, clay and active zinc oxide were used as fillers. In addition to these, the insulation mixtures contained small percentages of paraffin, mineral oil and Buna softener No. 32, as softening agents, although

TABLE II

ELECTRICAL AND MECHANICAL PROPERTIES OF EXPERIMENTAL N. G. A. CONDUCTORS

Property	Natural rubber	Buna S	Buna SS
Specific resistance of steam-vulcanized sheets (ohms per cm. $\times 10^{14}$)	20	7	13
Insulation resistance of the conductor (calculated in megohms per km.)	1800	700	1000
Insulation resistance of the conductor (measured in megohms per km.)	950	350	400
Insulation resistance of the conductor (after 12 weeks in air at 100° C)	600	1000	4000
Tensile strength of the rubber insulation (kg. per sq. cm.)	103	52	88
Elongation at break of the rubber insulation (percentage)	270	320	390
Tensile strength of the rubber insulation (after 1 week in air at 100° C)	92	57	92
Elongation at break of the rubber insulation (after 1 week in air at 100° C)	220	270	340
Tensile strength of the rubber insulation (after 12 weeks in air at 100° C)	0	52	83
Elongation at break of the rubber insulation (after 12 weeks in air at 100° C)	0	60	140

Buna S and Buna SS were plasticized chiefly by heat treatment (to 600 degrees on the Defo apparatus). The mixtures were vulcanized with sulfur and tetramethylthiuram disulfide as accelerator. They were then run on a strip-covering machine onto copper wire of 1.5 sq. mm. cross-section, with a wall thickness of rubber insulation of 0.8 mm. In accordance with the specifications of the V. D. E., the rubber insulation was composed of two layers of different colors. The dark layer contained a small percentage of active carbon black. The insulation resistance of the conductor was measured by means of 5-meter lengths in water at decreasing temperatures, with a 1000-volt direct current. The measurements were continued for 6 hours.

Table II compares the insulation resistances of strip-covered cables made from natural rubber, Buna S and Buna SS, and also the specific resistances of vulcanized sheets of the mixtures used in making the natural rubber, Buna S and Buna SS insulations for conductors. Taking into account the wall thickness of the insulation of the conductor, the relation between the specific resistance and the insulation resistance of this insulation was derived mathematically, and plotted as in Figure 4. From this diagram it is possible to obtain the theoretical values

of the insulation resistance of the conductor for any measured value of the specific resistance of the insulating mixture (it is best to choose the average value of the two layers), and to compare these theoretical values with the measured values. The theoretical values for the three experimental conductors are recorded in Figure 4. The measured values of these conductors are somewhat lower, and the straight lines representing these values enclose an area which is shaded in Figure 4, and within which fall the values of the majority of the conductors which were tested.

When a longer sample of conductor gave a result which differed considerably from the theoretical value, this was conclusive evidence that the mixture had been carelessly processed or was a difficult one to process. In conjunction with electrical breakdown tests, technical control tests of the uniformity of the processing operations proved once more their value in the development of mixtures for experimental conductors.

Figure 5 shows measurements of the temperature coefficients of insulation resistance of the experimental conductors. In this diagram, the insulation resis-

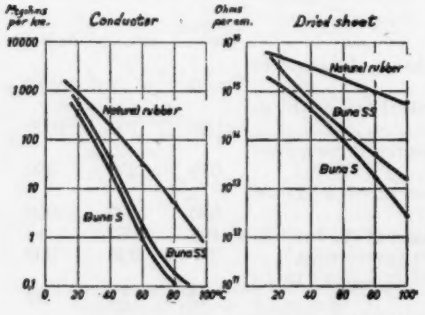

FIG. 5.—Insulation resistance and specifice resistance of the same material as a function of temperature.

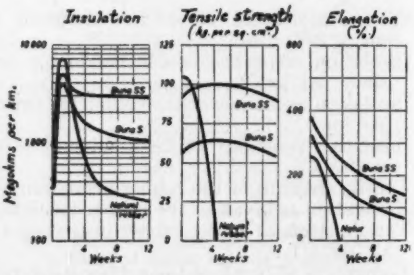

FIG. 6.—Aging of N.G.A. Conductors in Hot Air. (Mixture: crepe rubber, Buna S or Buna SS 100, sulfur 0.3, tetramethylthiuram disulfide 2.3, light magnesia 8, mineral oil 3, titanium dioxide 5, zinc oxide (active) 20, talc 70, whiting 70.)

tances of the experimental conductors, and also the measured specific resistances of the three mixtures from which the conductors were made, are shown as functions of the temperature. In this case the vulcanized sheets were dried before the measurements were made. The temperature coefficients of the various types of rubber in these technical mixtures differ in the same way as do those in the experimental mixtures.

Also of great importance in the practical evaluation of a rubber-insulated conductor are the mechanical properties of the insulation, for which the V. D. E. specify, for the conductor mentioned above, a tensile strength of insulation of 50 kg. per sq. cm. and 250 per cent elongation at rupture. As is well known, these values can be easily attained with an insulating composition containing 33 per cent by weight of natural rubber. As may be seen from the experimental results in Table II, it is possible, as a result of developments in methods of thermal softening, also to meet this specification with Buna S mixtures. It is still easier to obtain this tensile strength and elongation with Buna SS, because this type of Buna gives higher tensile strengths in mixtures containing no carbon black than does Buna S under the same conditions.

In brief, then, it can be asserted that it is possible to meet the specifications of the V. D. E. with rubber-insulated conductors containing 33 per cent by weight

of Buna S or Buna SS. Buna SS gives particularly good mechanical properties. The insulating properties of Buna S and of Buna SS are somewhat poorer than those of natural rubber. All these facts apply to new conductors ready for use.

Final judgment of the quality of an insulating jacket depends, however, on its behavior in service. Since this insulation is exposed to heat generated in the conductor by the electric current, the aging properties of this insulation in hot air are the best criterion of its value in service. Accordingly samples of the experimental insulated conductors were aged in hot air at 100° C for 12 weeks. These tests showed the great superiority of the Buna insulation over the rubber insulation. The superior insulating properties of natural rubber at the beginning declined so that at the end of only 2 weeks they were inferior to those of Buna S and Buna SS. The deterioration in tensile strength of the natural rubber insulation progressed so rapidly that at the end of about 5 weeks it had become very low, whereas both Buna S and Buna SS had not fallen below the specified value

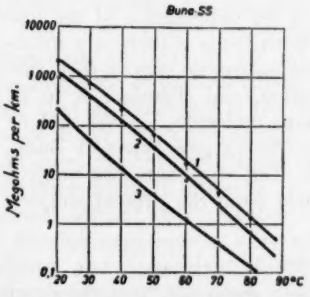

FIG. 7.—Insulation resistance of N.G.A. conductors as a function of temperature.

1. Unvulcanized.
2. Vulcanized in hot air 65 min. at 138° C.
3. Vulcanized in steam 40 min. at 138° C.

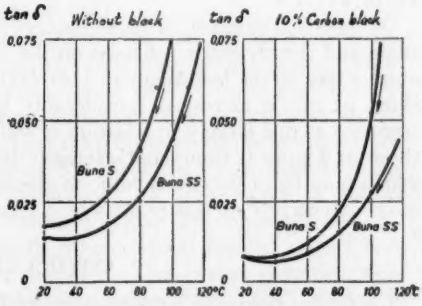

FIG. 8.—Loss factor as a function of temperature. (1000 volts, 50 cycles.)

of 50 kg. per sq. cm. of the V. E. D., even after 12 weeks. The elongations at rupture of the natural rubber, Buna S and Buna SS insulation decreased progressively with increase in the time of aging in hot air, and here too the two Buna rubbers were superior to natural rubber.

It will be noticed in the right-hand diagram of Figure 5 that thorough drying of insulation stocks vulcanized in sheet form in steam increased greatly their specific resistances. This is also indicated by the sharp increase in the insulation resistance of the experimental conductors during aging in hot air (see Figure 6), which in its initial stage represents a rapid drying.

The next step was, therefore, to vulcanize one of the experimental conductors in hot air instead of in steam, and to measure its insulation resistance, both before and after vulcanization. The results of these measurements for a 33 per cent Buna S conductor insulation are given in Figure 7. It is evident that vulcanization in steam reduces the insulation resistance of the conductor almost to one-tenth of its original value, whereas vulcanization in hot air has relatively little effect on the insulation resistance. Naturally in this case the freely exposed conductor will take up moisture again in the course of time.

DIELECTRIC PROPERTIES

Not only the specific resistance of a raw material for the manufacture of insulation of cables, but also its dielectric properties—loss angle and dielectric constant—are of interest, particularly in connection with low current service. It is important to know in what way these properties change with increase in temperature and with increase in frequency of the alternating current. Figure 8 shows the loss factors as a function of the temperature between 20° and 100° C, with a 50-cycle alternating current for the Buna S and Buna SS insulation mixtures, used on the experimental conductors already described. Again the superiority of Buna SS over Buna S in insulation resistance is evident. Also it can be seen that small proportions of active carbon black, in this case 10 per cent by weight of CK-3 black, improve the loss angle. This is of importance in a practical way because high mechanical strength of the insulation can be had without detriment to the dielectric properties. Within this range of temperatures the dielectric constant changed only slightly, and was of the order of magnitude of 4.3 to 4.7.

Of technical interest in high-frequency problems is the dependence of the loss angle and the dielectric constant on the frequency. With Buna S there is a maximum value of the loss angle at 1,000,000 cycles. This maximum occurs with raw Buna S, and is increased considerably by vulcanization, and therefore is to be regarded as due largely to addition of sulfur to the Buna molecule. Curves such as those in Figure 9 show characteristic differences for the various types of Buna, which may be of potential value in chemical analysis. But to go into this subject more extensively at this point would lead too far afield from the present subject.

CONDUCTIVE BUNA

Up to this point the various types of Buna have been discussed from the point of view of their use as raw materials with high insulating and dielectric properties for cable manufacture. It seemed desirable at this point to make efforts to obtain electrically conducting types of rubber. Perbunan in particular as a semiconductor seemed to offer possibilities in this respect.

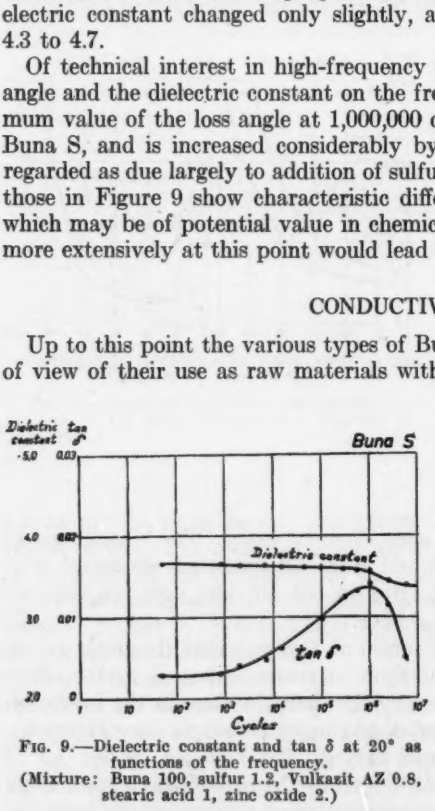

FIG. 9.—Dielectric constant and tan δ at 20° as functions of the frequency.
(Mixture: Buna 100, sulfur 1.2, Vulkazit AZ 0.8, stearic acid 1, zinc oxide 2.)

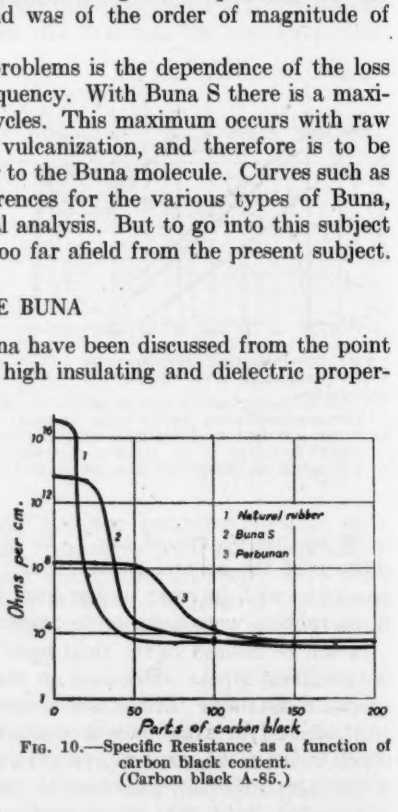

FIG. 10.—Specific Resistance as a function of carbon black content.
(Carbon black A-85.)

In high tension technique, for example, rubber mixtures are used today for spark plug conductors for screening and as a protection against corona, in order to prevent the formation of ozone, which is so harmful to rubber.

In general the electric conductivity of rubber mixtures is increased by carbon black, and this brings up the question as to what types of carbon black impart the greatest conductivity, how great a proportion of carbon black should be used to obtain any desired conductivity, and how the various types of rubber behave with such additions of carbon black. It was natural first of all to compare natural rubber, Buna S and Perbunan to obtain an idea of the way in which their specific resistances change with increase in the proportion of carbon black. Figure 10 shows the specific resistances of natural rubber, Buna S and Perbunan as functions of the proportion of the semiactive carbon black A-85. The experimental mixtures were vulcanized with sulfur and the accelerator Vulkazit AZ, but with no other compounding ingredient.

All three curves in Figure 10 are characterized by three distinct sections. In the first zone, the addition of carbon black did not cause any diminution in the specific resistance, but rather a slight increase. In the next zone, the specific resistance diminished rapidly with increase in the proportion of carbon black, until, in the third and last zone, saturation was apparently reached, so that the specific resistance approached a final constant value.

The three types of rubber, natural rubber, Buna S, and Perbunan are distinguished particularly by their behavior in the first and second zones. Thus, the first zone of natural rubber is the narrowest of all, that of Buna S is broader, and that of Perbunan is the broadest. These differences are of practical importance in insulation problems because they show that Buna mixtures for insulation can carry greater percentages of reënforcing carbon black than can natural rubber mixtures without lowering the insulation resistance. All three types of rubber tended toward an end value which lay between 10^3 and 10^4 ohms per cm.

Similar experiments were carried out with other carbon blacks, *e. g.*, CK-3, Elastic and Anacarbon 40-498 and flaked graphite. The curves obtained were of substantially the same character as those for carbon black A-85, shown in Figure 10. Furthermore there were no significant differences in the results, which depended on whether the measurements were made when the sheets were damp or after they had been dried.

Since relatively high percentages of carbon black A-85 are necessary to lower the specific resistance of Perbunan, various types of black were tested to determine whether better results might be obtained with other blacks. Figure 11 shows the influence of increasing percentages of various types of black on the specific resistance of a particular type of rubber, *viz.*, Perbunan. In this case the mixtures selected contained, in addition to various proportions of carbon black, 25 parts by weight of softeners (Aldol Resin, Alkydal and Plastikator 77). The general trend of the curves was not altered by the addition of these softeners. From a practical point of view, this is important in the successful extrusion of conducting Perbunan cable coverings. The comparative results, recorded graphically in Figure 11, show that different types of carbon black impart different properties to Perbunan. If the problem is, for example, to obtain a conductive Perbunan mixture with a specific resistance of 10^5 ohms per cm., the following proportions of the various carbon blacks would be necessary.

An electrically conducting rubber mixture is of permanent practical value only if its conductivity is not destroyed at elevated temperatures or by aging. In view of this, the temperature coefficients of conductive mixtures containing active carbon black CK-3, as a representative carbon black, were determined. The results, recorded in Figure 12, show that, above 50 parts by weight of carbon black, the conductivity was practically independent of the temperature. It is gratifying to find an electrically resistant material which behaves in this way.

Also aging of these carbon black mixtures in air at 100° C had little effect, as is evident in Figure 13.

Since elevated temperatures and aging have, from a practical point of view, but little influence on the specific resistance of highly loaded carbon black mix-

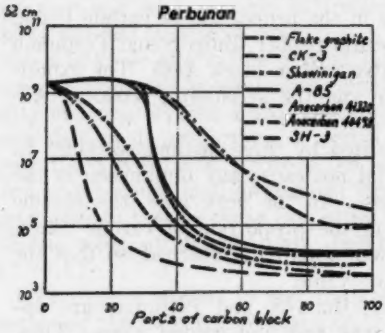

FIG. 11.—Specific resistance as a function of loading with various carbon blacks. (Mixture: Perbunan 100, sulfur 1.3, Vulkazit AZ 1, Aldol Resin 5, Alkydal STO 10, Plasticizer no. 77 10, zinc oxide 5, carbon black 0 to 100.)

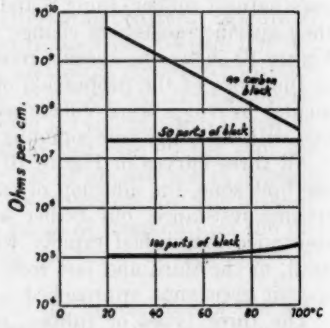

FIG. 12.—Specific resistance as a function of temperature. (Perbunan and carbon black CK-3.)

Black	Parts by weight
SH-3	18
Anacarbon 40-498	35
Anacarbon 40-320	40
Shawinnegan	43
A-85	48
Flake graphite	85
CK-3	above 100

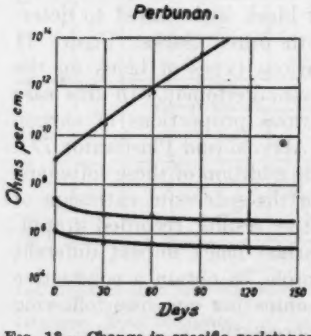

FIG. 13.—Change in specific resistance with aging in air at 100° C. (Perbunan with carbon black CK-3.)

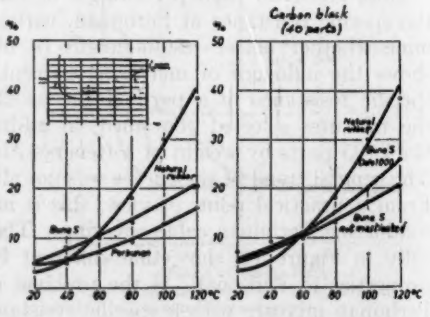

FIG. 14.—Residual deformation after application of a load as a function of temperature. (Mixture: rubber or Buna 100, sulfur 0.8 to 1.5, Vulkazit AZ 0.8 to 1.3, zinc oxide 5, carbon black CK-3 40.)

tures, it was decided, as a final experiment, to determine whether mechanical stress might have some influence on the specific resistance. This part of the work is however not yet completed, and will not be described here.

WATER ABSORPTION AND PERMEABILITY TO WATER VAPOR

A constant danger to the insulation resistance of conductors and cables is penetration of moisture. Efforts have therefore been made to develop insulating mixtures which absorb as little moisture as possible, and particularly in the case of cables with no lead covering, the effort has been to protect the insulating layer by a cable covering which allows the least possible amount of moisture to pass through it. Permeability to water and absorption of water are, therefore, properties which serve as criteria of the behavior of rubber mixtures exposed to moisture.

The permeability to water vapor of a series of organic raw materials has been determined by Taylor, Hermann and Kemp[1] and by Badum[2]. Using the same method of measurement in the present work, the permeabilities of various types of rubber in the original untreated state and after being compounded and vulcanized were determined and compared. These measurements were made on sheets, 1 mm. thick and 70 mm. in diameter, at 20° C in a current of air at 95% humidity. The results of measurements of four samples were averaged. The sheets contained a low percentage of zinc oxide and stearic acid, and were vulcanized with sulfur, with Vulkazit AZ as accelerator.

Mixture used for the measurements recorded in Tables III, IV, and V.

Rubber or Buna	100
Sulfur	1
Vulkazit AZ	1
Stearic acid	2
Zinc oxide (active)	5
Carbon black	0, 25 and 50

TABLE III

PERMEABILITY TO WATER OF VARIOUS TYPES OF RUBBER

Type of rubber	$\left(\frac{\text{g. of water}}{\text{h.} \cdot \text{sq. cm.} \cdot \text{cm. (mm. Hg)}} \times 10^{-8}\right)$ Raw material	Vulcanized material		
		Not compounded	P-33 black 25	P-33 black 50
Natural rubber	27.0	6.2	4.8	4.7
Buna S	18.6	12.9	9.9	7.8
Buna SS	8.1	5.1	4.2	3.4
Perbunan	28.1	17.6	15.1	12.6
Perbunan-Extra	21.2	13.6	10.7	9.5

Table III shows first of all the permeability to water of the different types of rubber in the raw, uncompounded state. It is evident that Buna S, Buna SS and Perbunan-Extra are less permeable to water than is natural rubber, which is superior in this respect only to Perbunan.

The results were far different when natural rubber was masticated, and also when all the different types of rubber were both masticated and vulcanized. Under these conditions natural rubber was superior also to Buna S (which had not been thermally softened) and to Perbunan-Extra. On the other hand Buna SS retained its superiority as the type of rubber with the lowest permeability to water. The same order was maintained when the proportion of P-33 carbon black was increased, although in all cases the actual permeability to water diminished in proportion to the increase in P-33 black. Consequently permeability to water can be diminished by loading a rubber mixture with carbon black.

In what fundamental way the different types of rubber differ with respect to their permeability to vapors and to gases can be seen from the comparative data in Table IV. Whereas, for example, Perbunan (vulcanized but not loaded) was 2.8 times as permeable to water as was natural rubber, the permeability of Perbunan to gas was less than 20 per cent that of natural rubber.

Furthermore, a comparison of the data in Table V shows that there was no simple relation between permeability to water and water absorption. The swelling in water was measured as percentage gain in weight by sheets 1 mm. thick and with a surface of 100 sq. cm. at 20° C after 100 days' absorption. It is evident that Buna S was decidedly superior, and Buna SS slightly superior, to natural rubber.

TABLE IV

COMPARISON OF THE PERMEABILITY TO WATER VAPOR AND TO GAS OF VULCANIZED BUT NOT LOADED SHEETS

Type of rubber	Permeability to water vapor $\left(\frac{\text{g. of water}}{\text{h.} \cdot \text{sq. cm.} \cdot \text{cm. (mm. Hg)}} \times 10^{-8}\right)$		Permeability to gas $\left(\frac{\text{cc. of air}}{\text{h.} \cdot \text{sq. cm.} \cdot \text{cm. (mm. Hg)}}\right)$	
Natural rubber	6.2	100%	3.4	100%
Perbunan	17.6	280%	0.6	18%
Buna S	12.9	210%	5.3	156%
Buna SS	5.1	82%	..	...

TABLE V

COMPARISON OF THE WATER ABSORPTION AND PERMEABILITY TO WATER OF VULCANIZED BUT NOT LOADED SHEETS

Type of rubber	Water absorption (% by weight)	Permeability to water vapor $\left(\frac{\text{g. of water}}{\text{h.} \cdot \text{sq. cm.} \cdot \text{cm. (mm. Hg)}} \times 10^{-8}\right)$
Natural rubber	6.5	6.2
Buna S	4.5	12.9
Buna SS	6.0	...
Perbunan	7.5	17.6
Perbunan-Extra	7.2	13.6

In the light of these results a survey of the properties of the different types of rubber which have a determinant influence on the insulating value of the rubbers seems to point to Buna SS as well as to Buna S as being particularly suitable for insulating mixtures in cable manufacture. High specific resistance, good processing of mixtures containing no carbon black, excellent aging properties, and slight sensitivity to moisture justify this opinion of the value of Buna SS and Buna S.

RESISTANCE TO COMPRESSION OF CABLE COVERINGS

Some work has also been done on the particular mechanical properties of different types of Buna which are of importance in the manufacture of cables. In this case insulating mixtures were tested. The mechanical properties required of mixtures for cable covering are still more exacting, and extend over a wide range of temperatures.

The resistance of cable coverings to compression is of importance both at ordinary temperatures and at elevated temperatures. Cable coverings made from natural rubber, Buna S and Perbunan were compared in this respect, under

the same conditions of mixing, etc. The mixtures chosen contained, in addition to small percentages of zinc oxide and stearic acid, 40 per cent of active CK-3 carbon black, a type of composition which is widely used for extruded cable coverings of high mechanical strength. The mixtures were vulcanized with sulfur and Vulkazit AZ.

The resistance to compression was measured on cylindrical test-specimens 40×40 mm., at temperatures from 20° to 120° C. The semipermanent deformation (the "residual deformation" of specification E-3510 of the D. V. M.) was measured 1 minute after release from a load of 10 kg. per sq. cm. for 5 days. The results are shown in Figure 14, and are expressed as percentages of the original height.

The upper part of the left-hand diagram in Figure 14 shows the deformation as a function of time. When the residual deformation was plotted as a function of temperature, the curves shown in Figure 14 were obtained. The slopes of these curves are an indication of the thermoplasticity of the mixtures. The steeper the slope of a curve, the more thermoplastic was the mixture. From this point of view, it is evident that natural rubber is decidedly more plastic than either Buna S or Perbunan. As a result, the residual deformation of natural rubber around 60° C became greater than the residual deformations of Buna S

TABLE VI

RESIDUAL DEFORMATION

(Percentage)

Temperature	Perbunan	Buna S	Buna S (thermally softened)	Natural rubber
20° C	5	5	7	4
80° C	10	13	15	19
120° C	16	20	26	38

and Perbunan. On the other hand, at ordinary temperature the residual deformations of the two Buna rubbers were somewhat higher than the deformation of natural rubber, because with such a short time between release of the load and measurement of the deformation, the lower rates of flow of the two Buna rubbers played a noticeable part in the effects. This may be seen from the data in Table VI.

The curves in the right-hand diagram of Figure 14 show the effect of thermal softening on the residual deformation of Buna S. An interesting result and one which was to be expected is that the residual deformation was increased somewhat by preliminary thermal softening, but that the slope of the curve was not materially increased. Buna S is not, therefore, rendered essentially more thermoplastic by thermal softening, and even after this latter heat treatment it is superior, as before, to natural rubber in this respect.

RESISTANCE TO COLD

To express quantitatively the resistance of cable covering mixtures to cold, a problem which is becoming of increasing practical importance[3], it is better to choose the modulus of elasticity rather than the residual deformation, for the modulus of elasticity is an indication of brittleness, and this latter property may be an important feature of a cable covering at low temperatures.

Two extruded Perbunan mixtures[4] were chosen as examples to illustrate this point. The two mixtures were of exactly the same composition except for dif-

ferent percentages of a softening agent (Plasticizing agent no. 77). For measuring the compression moduli of these mixtures, cylinders 40×40 mm. were subjected to a static load of 5 kg. per sq. cm. for 24 hours at different temperatures. It is evident from Figure 15 that the mixture containing only 15 per cent by weight of softener became rapidly and progressively harder at temperatures below −20° C, whereas the mixture containing 75 per cent of softener did not become appreciably more brittle even at temperatures as low as −50° C. For the coverings of portable cables, which in mines for example are subjected to severe wear from abrasion, the relatively high resistance to abrasion of Buna cable coverings is obviously an advantageous property. Although practical methods for testing cable coverings are still to be developed, they are certain to show Buna to as favorable an advantage over natural rubber as they have done in test of tires, in which case Buna has shown a 30 per cent superiority over natural rubber.

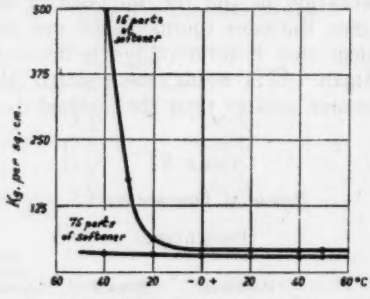

FIG. 15.—Elastic modulus as a function of temperature.
(Mixture: Perbunan 100, sulfur 1.5 Vulkazit 1.3, zinc oxide 5, resin 2, Plasticizer no. 77, 15 and 75, carbon black CK-3 10, 3-FCHM 20.)

Development work in the cable industry in the last few years, which has been similar in character to the experimental investigation described in the present paper, has, by solving many fundamental problems, laid the basis for the successful use of Buna in this industry.

REFERENCES

[1] Taylor, Hermann and Kemp, *Ind. Eng. Chem.* **28**, 1255 (1936).
[2] Badum, *Kautschuk* **14**, 231 (1938).
[3] Stöcklin, *Kautschuk* **15**, 118 (1939).
[4] The mixtures from which the curves in Figures 5, 11 and 15 were obtained were developed by Dr. Gartner, Leverkusen.

LITERATURE ON BUNA IN THE MANUFACTURE OF CABLES

[1] Röhrs, Staudinger and Vieweg, "Fortschritte der Chemie, Physik und Technik der Makromolekularen Stoffe", Lehmanns Verlag, München-Berlin, **1939**.
[2] Boström, Lange, Schmidt and Stöcklin, "Kautschuk und verwandte Stoffe", Union Deutsche Verlagsges., Berlin, Roth and Co., **1940**.
[3] Boström, Types of mixtures for the production of rubber conductors and cables, *Gummi-Ztg.* **1939**, 1030, 1048.
[4] Breitenstein, Marine cables with artificial materials, *Kunststoffe* **1940**, 29.
[5] Konrad, The synthetic rubber Buna, *Jahrbuch der Deutschen Luftfahrtforschung* **1938**, 574.
[6] Breitenstein, Electrical equipment on naval vessels, *Elektrotech. Z.* **1939**, 840.
[7] Nowak, Introduction of high-polymeric artificial substances into cable and conductor construction and subsequent developments in their use for this purpose, *Kunststoffe* **1939**, 192.
[8] Roelig, Buna S for the manufacture of cables and for hard rubber, *Kunststoffe* **1939**, 47.

[9] Viehmann, Conductors, electric terminals and radio interference in aeronautics, *Jahrbuch der Deutschen Luftfahrtforschung* **1938**, 1311.
[10] Nowak and Hofmeier, The effect of rubberlike high polymers on the physical properties of Buna mixtures, *Kautschuk* **1938**, 193.
[11] Pfestorf and Hetzel, The electrical properties of artificial materials as a function of temperature, *Elektrotech. Z.* **1938**, 875.
[12] Badum, The permeability of organic raw materials to water, *Kautschuk* **1938**, 231.
[13] Badum, The use of Buna as insulation for ocean cables, *Proc. Rubber Tech. Conf. London*, **1938**, Paper No. 40.
[14] Heering, High voltage rubber cables, *Proc. Rubber Tech. Conf. London*, **1938**, Paper No. 84.
[15] Ludendorff, Insulated conductors and cables of new compositions. Experiments with German raw materials by the German Government railways. *V.D.E. Fachberichte*, **1938**, 128.
[16] Roelig, Buna in electrotechnology, *V.D.E. Fachberichte*, **1938**, 125.
[17] Bormann, Experiences with rubber as insulation for high voltage conductors and cables. *Elektrotech. Z.* **1938**, 960.
[18] Nowak and Hofmeier, Synthetic high polymers as raw materials in cable and conductor construction, *Kunststoffe* **1938**, 54.
[19] Nowak, Development of artificial materials in the field of cables and conductors, *Kunststoffe* **1938**, 39.
[20] Roelig, Buna in the manufacture of cables, *Elektrotech. Z.* **1938**, 172.
[21] Nowak and Hofmeier, New artificial materials in the electrical industry, particularly for cable and conductor construction, *Kunststoffe* **1937**, 184.

EFFECT OF OPERATING CONDITIONS ON THE LIFE OF RUBBER BELTS *

R. J. PERIN

The variation in life of rubber belting has been a major technical problem of the rubber industry for many years. Although rubber compounds have been greatly improved, both in flexing life and aging properties, the life of belts on certain types of drives has not increased accordingly. To determine the cause of this variation, a survey was made of the performance records of belts on all types of drives. From this survey it was possible to obtain data on those drives wherein the belt life fell below the average expectancy. An analysis of this information divided these premature failures into two groups, which were designated as "external" and "internal". The former classification includes failures due to excessive slip, high temperatures, misalignment and other detrimental operating conditions. The latter group includes those failures with no signs of external damage, and where failure involves that common condition, internal separation of the plies.

A further examination of the reports on internal failures showed that practically all the drives concerned had one or more of the following characteristics: small pulley diameters, high belt tension, or high belt speed. The problem then resolved into a determination of the relative effect of these conditions on belt life.

It was decided to evaluate, by laboratory experiment, the effects of these variables on the rate of ply separation, and thus to obtain an index as to the relative belt life. The variables which were included in the investigation were pulley diameter, belt tension, belt thickness and belt speed. These factors were studied individually and also in various combinations.

Two types of machines were used throughout these experiments: first, a 75-horsepower dynamometer of conventional type, comprising an electric motor on slide rails, with a suitable means of applying tension in the test belt, and a pivoted brake loaded drum, water cooled, with adjustable loading device to maintain a constant load; secondly, a multiple head machine, each unit consisting of a driver pulley in a fixed mounting overhead, an idle driven pulley of equal diameter, mounted in vertical ways directly below the driven pulley, and means to suspend variable weights from the idle pulley to secure desired belt tension.

The first machine was used for power transmission tests and the second for those without load. Both machines were designed to accommodate a wide range of pulley diameters, tensions and speeds. All the pulleys had standard crown faces.

Two lengths of belting were used to provide the test-specimens. Belt A was a 6-ply belt and tested as such. Belt B was an 8-ply belt, and for tests of less than 8-ply thickness one or more of the plies were removed as required, starting from the pulley side. Thus comparable specimens of 4, 5, 6, 7 and 8 plies were obtained without introducing the variable of belt quality.

The end point of the test was taken as the time when ply separation had extended for 5 inches along the length of the belt. The reason for this standard 5-inch length was the obvious impracticability of inspecting the test belts often enough to find the exact moment of initial separation. Permitting the ply sepa-

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ration to extend to a definite distance along the belt gave an opportunity accurately to fix the end point of the test.

The results obtained will first be shown as related to the individual variables and later grouped as a whole.

Pulley Diameter.—It was found that the following statement was applicable. The hours to separate the plies of the belt varied directly with the pulley diameter to the 5.35 power. Figures 1 and 2 illustrate the effect of this variable in combination with selected tensions. The points located on or adjacent to the lines in all the figures are actual test results, each point being the average of three individual tests. The actual results obtained are of interest, thus (Figure 1) one test on 6-inch pulleys with 9 lbs. tension per ply-inch gave a flexing life of approximately 90 hours, whereas the same tension over 8-inch pulleys gave a flexing life of 400 hours. In other words, an increase of 33⅓ per cent in pulley diameter resulted in a 450 per cent increase in flexing hours. The difference between the position of the comparable lines in Figures 1 and 2 may be attributed to a difference in belt quality. It should be noted, however, that the shape of both sets of curves corresponds to the formula. Figure 3 also shows the effect of varying pulley diameters, this time in combination with various plies. Here a 6-ply belt over 6-inch pulleys gave 60 hours flexing life, compared with 900 hours over 10-inch pulleys.

Tension.—It was possible to establish the following relation between hours to ply separation and tension. The hours to separate the plies of the belt varied inversely as the tension per ply inch to the 4.12 power. Figure 4 is based on the same data as Figure 1, with tension replacing pulley diameter as the ordinate axis. A test belt running over 8-inch pulleys gave a 400-hour life at 9 lbs. tension, dropping to 50 hours at 15 lbs. tension.

Belt Thickness.—Here the following statement applied. The hours to separate the plies of the belt varied inversely as the thickness to the 6.27 power. Figure 3 graphically represents this factor.

Belt Speed.—The following formula was developed for this variable. The hours to separate the plies of the belt varied inversely as the speed to the 0.5 power. These data are shown in Figure 5.

From the individual factors listed above the following general formula may be deduced:

$$H = K \frac{D^{5.35}}{S^{0.5} N^{6.27} T^{4.12}}$$

where H = Number of hours to obtain a ply separation of 5 inches.
K = Numerical factor, depending on belt quality, belt length and other possible factors not studied in this test.
D = Pulley diameter in inches.
S = Belt speed in feet per minute.
N = Number of plies.
T = Tension in the belt in lbs. per ply-inch.

As explained previously, two different types of machine were used to make the tests from which the above formula was derived. One was a dynamometer, and the other simply flexed the belt under tension without load. It was considered advisable to determine whether or not the use of two different methods of test introduced further variables. Therefore comparable tests were made on lengths of belting on the two units. The results of these are shown in Table I.

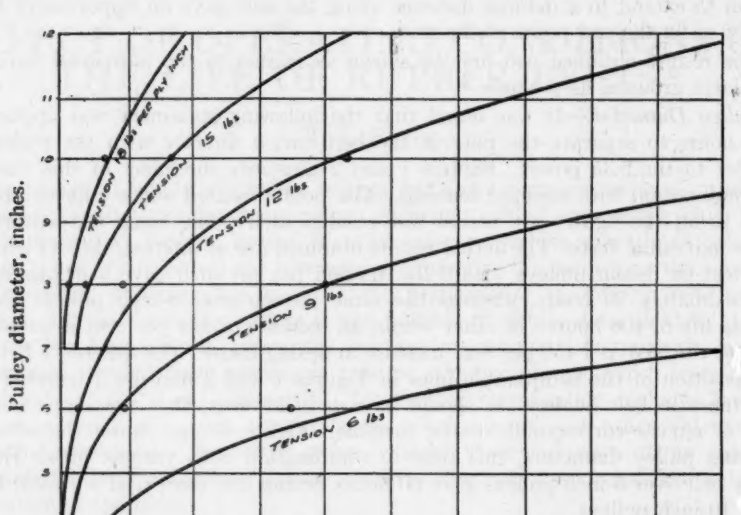

FIG. 1.—Result of tests on Belt A, 6 ply, with 1500 ft. per min. belt speed.

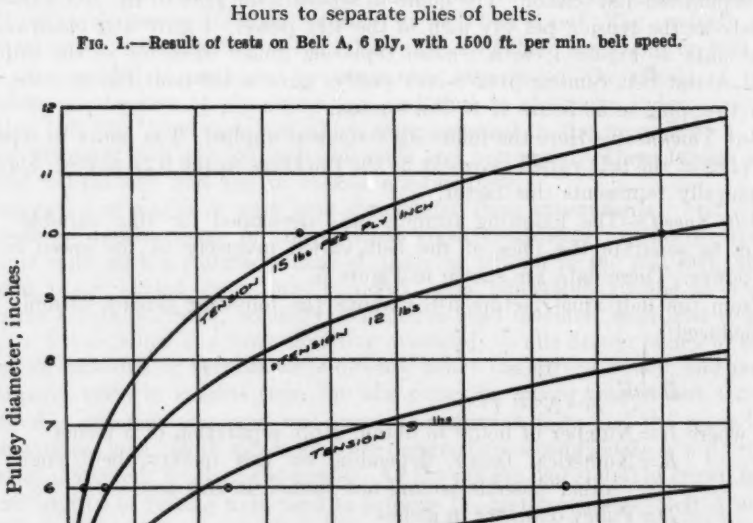
Pulley diameter, inches.
Hours to separate plies of belts.
TENSION 15 lbs PER PLY INCH
TENSION 12 lbs
TENSION 9 lbs
TENSION 6 lbs

FIG. 2.—Results of tests on Belt B, 6 ply, 1500 ft. per min. belt speed.

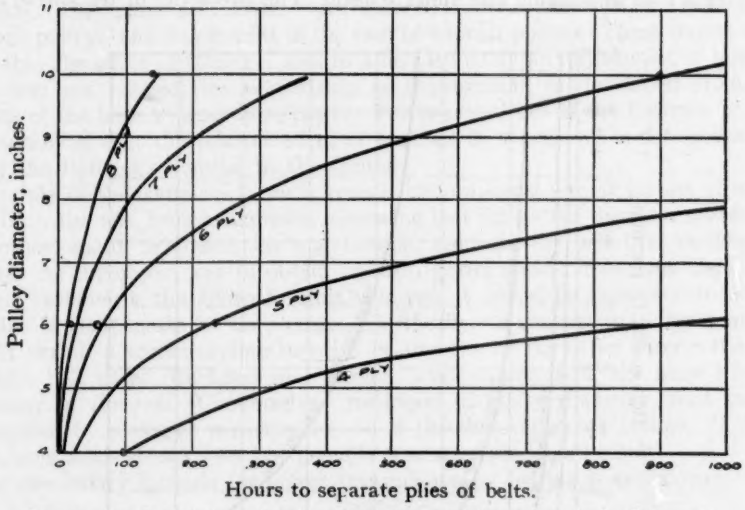

FIG. 3.—Result of tests on Belt B with tension of 12 lbs. per ply inch. Belt speed 1500 ft. per min.

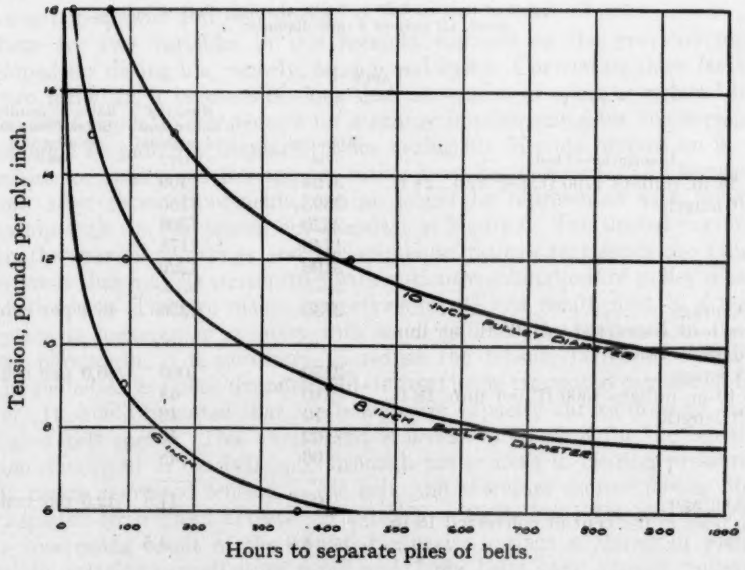

FIG. 4.—Result of tests on Belt A, 6 ply with 1500 ft. per min. belt speed.

It will be noted that the change from 18-inch to 10-inch pulleys reduced the number of hours by approximately the same percentage, whether the belt was carrying a load or running idle under tension. The two series of tests were made

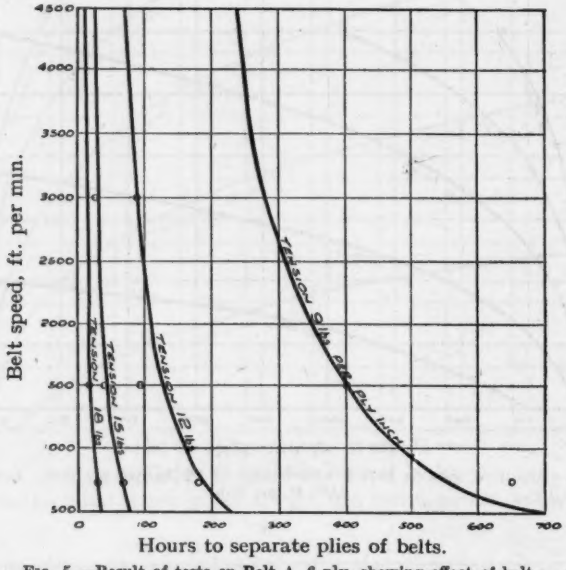

FIG. 5.—Result of tests on Belt A, 6 ply, showing effect of belt speed, all pulleys 8-inch diameter.

TABLE I

Description of test	Running idle	Running under load (dynamometer)	Ratio of results in load tests to running-idle tests
Two 18-in. pulleys 1700 ft. per min., 24 ft. belt length.	3794	1400	
	2393	1156	
	2520	1300	
	1746	1176	
	3196	1220	
Average	2730	1250	46.0 per cent
Above tests converted to 1500 ft. per min. and 18 ft. length.			
Average	2170	1000	46.0 per cent
Two 10-in. pulleys 1500 ft. per min. 18 ft. belt length	110	48	
	110	43	
	102	40	
	100	48	
Average	105.5	44.8	42.5 per cent
10-in. tests in per cent of converted 18 in. tests	4.9	4.5	

with belts of different lengths, but assuming that the length is a first-power function, and making a correction for the slight difference in speed, it will be seen that when the belt was running idle the hours were reduced to 4.9 per cent, and when carrying a load the hours were reduced to 4.5 per cent. The amount

indicated by the formulas is 4.3 per cent. This close relationship is well within the limits of experimental error.

The effect of adding a load to the belt was practically the same on both series of tests. The number of hours were reduced to 42.5 per cent in the case of 10-inch pulleys, and 46 per cent in the case of 18-inch pulleys. These results indicate that the effect of adding a load to a belt is merely an adjustment of tension, and does not change the relationship in the formula as developed from the results of the tests without horsepower. For practical use of the formula, it may be considered that the relative effect of tensions in two drives is determined by using the tight side tension in the formula.

A study of the complete formula reveals two opposing sets of factors affecting belt life: the one, pulley diameter, increasing belt life as the diameter increases; the other, speed, belt thickness and tension, reducing the belt life, as they increase. As the object was to obtain uniform performance, it became clear that as one variable in the above formula changed, it would be necessary to adjust another to compensate for the change. Specifically, an increase in pulley diameter would permit a corresponding increase in any one of the other three variables, namely, belt speed, thickness and tension, while maintaining the same life expectancy of the belt. Conversely a reduction in pulley diameter must be accompanied by a similar reduction in one of the three opposing factors. If, however, such adjustments were not possible, a shorter life would result.

An elementary formula for power transmission by belting is as follows:

$$\text{Horsepower} = \frac{\text{Belt speed} \times (\text{tight side tension-slack side tension})}{33{,}000}$$

Provided the difference in tension is constant, there is thus a linear relation between horsepower and belt speed.

There are two variables in this formula common to the previous formula developed for flexing life, namely, tension and speed. Correlating these factors in the two formulas, it becomes obvious that, as tension or speed is reduced in the flexing life formula to compensate for a change in other variables, the horsepower rating must be reduced. Similarly, if the flexing life formula permits an increase in tension or speed, the horsepower rating may be increased. The horsepower ratings, after these adjustments, can no longer be represented as a linear relationship with the belt speed, but is shown in Figure 6. The shaded portion between the maximum ratings and the minimum ratings represents the range of horsepower that may be transmitted with various combinations of pulley diameter and belt speed. The two major corrections introduced result, first, in a marked reduction in horsepower capacity with small pulleys. As explained in the preceding paragraph, it is necessary to reduce the tension factor to compensate for the reduction in pulley diameter, this in turn being translated to reduced horsepower. It should be noted that the horsepower capacity curves drop off sharply at higher belt speeds. This adjustment is necessary to allow for the centrifugal tension developed in the belt and, although not evident in bearing pressure, actually means increased tension in the belt, and therefore shorter flexing life unless adjusted by reduced horsepower capacity with its lower external tension.

An interesting result of the adjusted capacity ratings is shown in Figure 7. Here the relative capacities of 6-ply and 7-ply belts over 12-inch pulleys are shown. It will be seen that the 6-ply has a higher horsepower rating than the 7-ply belt. This difference is shown by the shaded area. This is due exclusively to the small pulley diameter involved, wherein the reduction of ply thickness compensates for the effect of the smaller pulley diameter.

Thus it has been shown that although the manufacturer of rubber belting may improve the resistance of the belt to ply separation by several times, as has been accomplished in recent years, the user of the belting has it within his

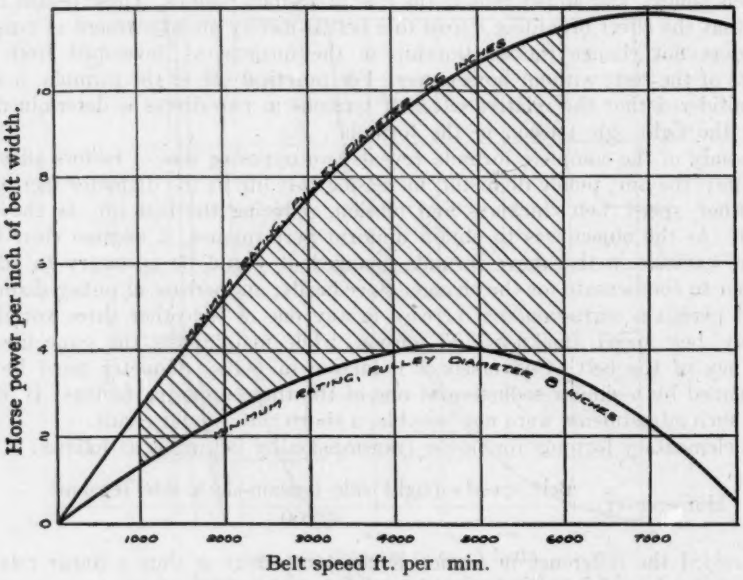

FIG. 6.—Revised belt ratings, 6-ply.

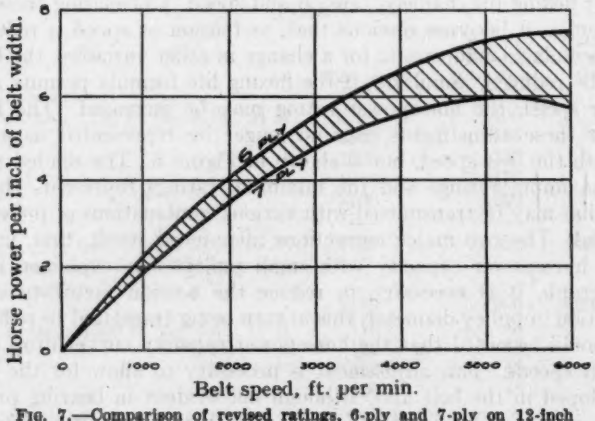

FIG. 7.—Comparison of revised ratings, 6-ply and 7-ply on 12-inch diameter pulleys.

power to increase or decrease the severity of the belt installation to a large extent by his selection of pulley size, tension, number of piles and speed. A radical revision of horsepower capacity recommendations is necessary to equalize the effect of these variables.

THE STANDARDIZATION OF DUROMETERS *

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The hardness test is one of the most useful and convenient physical tests which can be made on vulcanized rubber. It is easily made because the equipment can be simple, compact and portable. It is particularly useful in that the test sample may be a production article which can be put into service, undamaged, after the test. Consequently the test appears in the industry in several modifications, and the tester in diverse styles.

Several more or less readily portable hardness testers are available commercially. The Shore Instrument and Manufacturing Co. has its line of Durometers, types A, B, C, D, etc.; Schopper, through Testing Machines, Inc., has marketed a tester similar to the Shore type A; the U. S. Gauge Co. has an instrument of the same type using the case of their pressure gage; the Firestone Penetrometer is another well-known tester of the spring-load type, as is the Adams Densimeter. At the present time the Society's Committee D-11 on Rubber Products is studying four portable hardness testers which are based on the specifications of the Standard Method of Test for Hardness of Rubber (D 314-39)[1], three of these being spring-operated instruments, the fourth, a dead-load type. In addition to the testers mentioned above, there is the Pusey-Jones Plastometer, which is a dead-weight hardness tester rather than a plastometer.

Generally speaking, portable hardness testers are spring-operated. Beyond this feature, they have little in common with each other or with either the A.S.T.M. tester (D 314) or the Pusey-Jones Plastometer (D 531-39 T)[2]. Figure 1 gives an indication of the disparity of results obtained with some of these instruments.

The situation is little better when a comparison is made of several Durometers made by the same manufacturer, as can be seen in Figure 2, which shows the hardness of one sample of rubber, measured by 20 instruments which were in use in one factory. If the hardness of this compound were specified as 65 ± 2, which is a common tolerance, the sample would have been rejected by eight of the Durometers.

Further indications of the lack of agreement among Durometers may be found in the discussions of the Society's Committee D-11. It is evident that a technique of standardization is necessary and that the fundamental principles should be known to designers and users. This paper presents a résumé of the theoretical laws of penetration of a material such as vulcanized rubber, and their application in standardizing Shore Type A Durometers as an example of one of the widely used hardness testers. Suggestions are made for an improved type of hardness tester.

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* Transcribed from a preprint of a paper presented at the 43rd annual meeting of the American Society for Testing Materials, at Atlantic City, N. J., June 24-28, 1940.

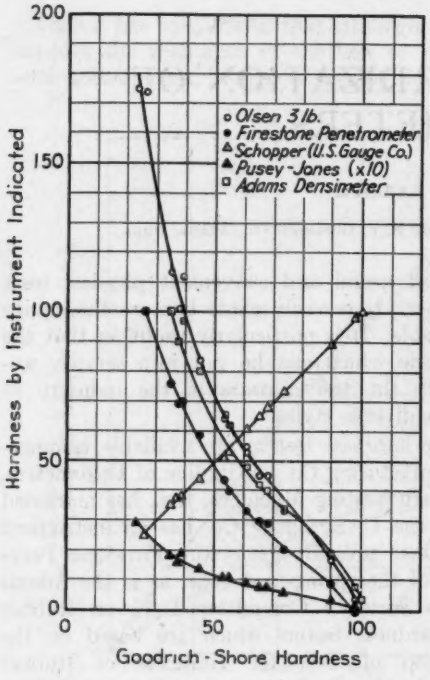

FIG. 1.—Interconversion of hardness readings.

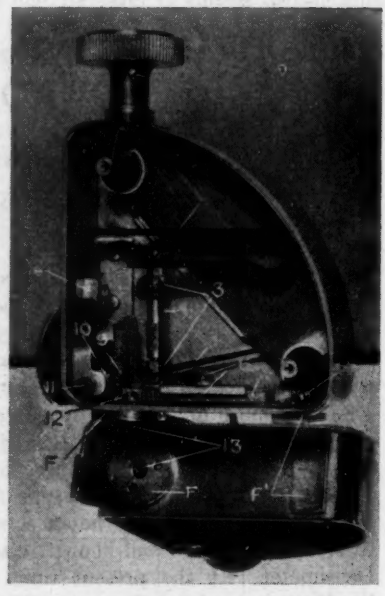

FIG. 3.—The mechanism of a Durometer.

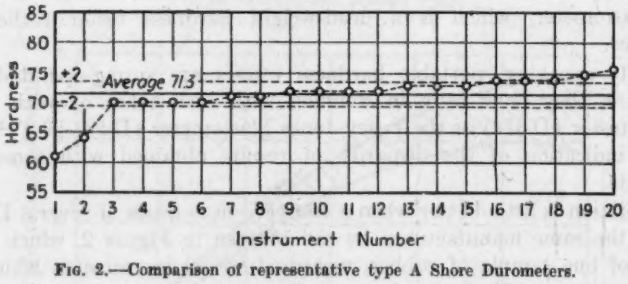

FIG. 2.—Comparison of representative type A Shore Durometers.

THEORETICAL BASIS

It has been found[3] that the penetration of vulcanized rubber by rigid spherical indentors follows the laws of classical elasticity for indentations as high as 10 per cent of the diameter of the indenting sphere. At 20 per cent the measured penetration is not much greater than that predicted by the theory. Theory and experiment show that:

1. If a rigid spherical indentor is pressed into an isotropic elastic material, the penetration d is proportional to the two-thirds power of the load L and inversely proportional to the cube root of the diameter D of the indentor, the proportionality factor containing the elastic moduli. For vulcanized rubber, where Poisson's ratio is 0.5, Young's modulus E can be determined by the relation:

$$d = (0.86/E^{\frac{1}{3}})(L^{\frac{2}{3}}/D^{\frac{1}{3}}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

2. The normal deflection of the surface of the rubber does not fall off rapidly with distance from the indentor, being 4 per cent of the maximum indentation at a distance from the indentor ten times the radius of contact a $(=\sqrt{(dD/2)})$. Therefore the indentor should be placed several times this distance from a free edge.

3. The compressive stress along the axis of penetration has dropped to 1 per cent of its initial value in a distance equal to ten times the radius of contact. Consequently the thickness of the sample should be this much.

4. The stress system at the center of contact is one of pure hydrostatic pressure.

5. The normal compressive stress, p, in the contact area at a distance, r, from the center is:

$$p=3L(a^2-r^2)^{\frac{1}{2}}/2\pi a \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where a is the radius of contact area. This is a maximum at the center and vanishes at the edge of contact.

The problem of penetration by a rigid cylinder was worked out early in the development of the elasticity theory. If a rigid right cylinder is pressed into a plane surface, the indentation is proportional to the first power of the load and inversely proportional to the first power of the diameter, the proportionality factor containing the elastic moduli. The normal compressive stress on the face of the cylinder:

$$p=L/2\pi a(a^2-r^2)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

becomes infinite at the edge instead of dropping to zero as it does with the spherical indentor.

THE STANDARDIZATION OF SHORE DUROMETERS, TYPE A

Shore has stated[4] that his specifications are as follows: "This instrument, in the absence of other specific demands made upon it with respect to calibration of the dial, has been originally provided with a simple metric scale. It has a frustum cone impresser pin $\frac{3}{64}$ inch in diameter, with the flat tip $\frac{1}{32}$ inch. The pin begins to yield and the indicator hand departs from zero after a prepressure of 2 ounces, then proceeding up to 29 ounces, at which point 100 is indicated on the dial. The total stroke of the pin is 0.1 inch, so that each division on the dial would stand for 0.001 inch of depth travel, which, while not regularly shown, would read inversely, that is, the zero for the depth travel would be at 100 on the scale, and 100 depth would be at zero of the adopted scale".

The Durometer is shown in Figure 3. As the indentor *13* is pushed into the case, rotating about *8* with respect to the case, the rack *9* turns the pinion *10* and carries the pointer *5* over the scale (not shown). Consequently the scale measures directly only the motion of the pin with respect to the case. This motion is resisted by the flexing of spring *1*, but the reaction of the spring through linkage *4* is not in the direction of motion of the impresser pin. Since the radius of the arc of rotation of the lower end of the linkage can be varied considerably by moving slide *6*, the load-deflection curve of the instrument is not necessarily a straight line. The "stress-strain" curve of the upper bearing *3* is determined by the geometry of spring *1* and by the material of the spring, but the region of this curve over which deflections of the pointer take place is determined by the length of linkage *4*, once the nut *2* has been securely locked.

As the instrument is pressed against a rubber surface by the knurled thumb-

rest at the top, the pressure of application is transferred to the rubber through the pin. In order that no lateral forces be applied to the pin, the rest plates F, F' must be parallel to the surface at all times. If the pressure is greater than that just necessary to define the plane of reference, the rubber will rise in the hole in F, carrying the indentor up with it to a falsely high hardness figure.

We see there are three adjustments—position of slide *6*, length of linkage *4*, and length of pin *13*—which may be made to change the hardness reading of a Durometer on a given sample. How does each of these adjustments influence the reading and the load-deflection relation? This question was answered by manipulation of a single Durometer. The effect of the first two adjustments was studied by moving slide *6* to the left and to the right of normal and by rotating the collar clockwise and counterclockwise, separately and in combination. Nine settings were thus made. These adjustments gave the variations in hardnesses on four samples shown in Table I. It can be seen that large changes

TABLE I

VARIATION IN READINGS OF TYPE A DUROMETER WITH ADJUSTMENTS OF COLLAR AND SLIDE

Adjustment	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4
1. Durometer adjusted to normal conditions....	22	34	70	97
2. Slide moved 0.02 in. to left of normal.....	21	32	68	96
3. Slide moved 0.02 in. to right of normal.....	24	36	70	96
4. Slide moved 0.08 in. to right of normal.....	33	45	75	97
5. Slide as in 4, collar turned two faces to right..	28	41	75	96
6. Collar as in 5, slide returned to normal position	19	31	69	96
7. Collar as in 6, slide moved 0.02 in. to left of normal	15	28	66	95
8. Slide as in 7, collar turned two faces to left...	25	36	71	97
9. Durometer returned approximately to normal adjustments	22	34	70	96

in hardness values of sample No. 1 were produced, but no significant change in value for sample No. 4. Because of the coarseness of the screw in the turnbuckle linkage and the roughness of the trunion arm, it is difficult to make these adjustments precisely.

While making these two adjustments the loads at four scale points were measured, Figure 4. Since the curves are all of the type: $y=mx+b$, it can be seen that by these two adjustments the load-deflection curve of a Durometer may be moved parallel to itself (change in b) or rotated (change in m) or, generally, may be given both translation and rotation. Figure 5 shows a non-linear load-deflection curve obtained when the slide adjustment was set far towards the left, as it has been found in Durometers received for calibration.

In considering the third adjustment, it should be noted that the length of pin protruding can have no effect whatever on the load-deflection curve, though it does change the hardness reading obtained with any given sample of rubber. If d is the penetration into the rubber (length protruding), in inches, and S the corresponding scale reading, it follows, from the geometry of the rack-and-pinion mechanism, that, neglecting the small departure from the straight-line motion of the pin:

$$d=K(S_0-S)=mK(L_0-L) \quad (4)$$

where:

K = a constant defined by the geometry of the mechanism;
S_a = the scale reading when the base of the pin is flush with the surface of the rest-plate;
m = the slope of the load-deflection line, and
L_a and L = the corresponding loads.

If the instrument were of the dead-load type the penetration from the reference plane (infinite hardness) would be independent of the length of indentor.

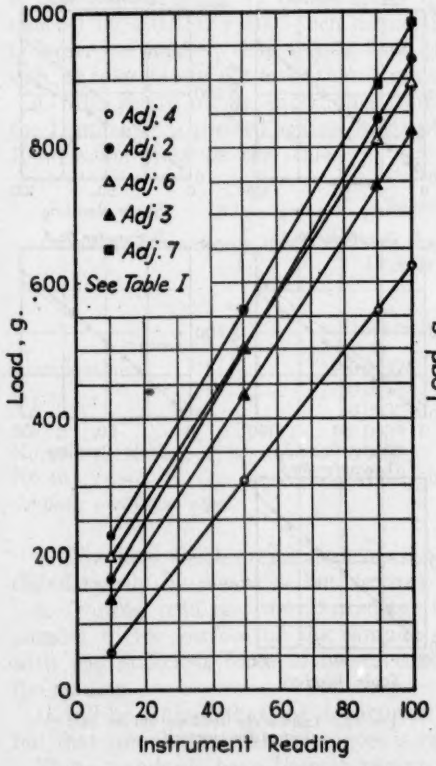

FIG. 4.—Typical load-scale reading curves.

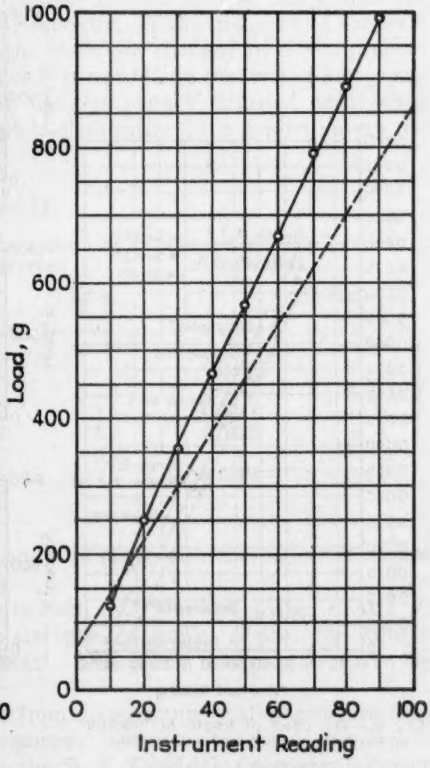

FIG. 5.—A non-linear load-scale reading curve.

In this Durometer, however, the applied load is nearly proportional to the movement of the indentor from its position at zero hardness, and the length of scale between zero and infinite hardness depends on the protruding length of indentor.

To determine the magnitude of the effect, a particular instrument was adjusted by changing the protruding length of indentor to read, successively, 95.5, 100, and 105 when pressed against a flat piece of plate glass. The hardness values of a series of rubber blocks were observed for each value of S_a and the penetration calculated by Equation 4, with the results shown in Figure 6. These data show that the hardness reading on any sample depends on the length of pin, and the variation in hardness readings from this cause is greatest at the

upper end of the scale. Therefore, this length must be specified with close tolerances.

The specifications quoted at the beginning of this section are not clear and there is no mention of tolerances. It must be inferred that a linear load-deflection curve is assumed by the manufacturer so that the two loads given shall uniquely determine the relation. That few Durometers in use comply with these simple specifications on load is shown by the data in Figure 7. Not one of these five instruments complied with the load specifications, all five having lower than

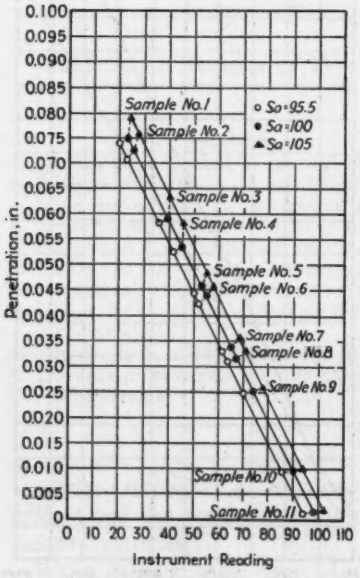

FIG. 6.—The effect of length of indentor on hardness readings and penetrations.

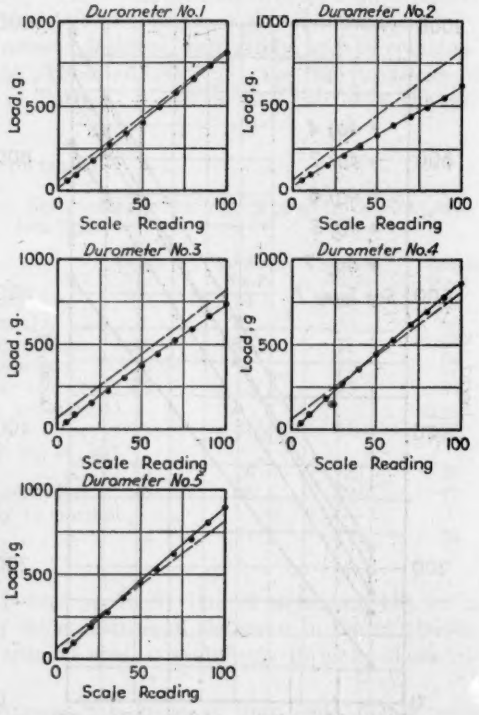

FIG. 7.—Load-scale reading curves of typical Durometers.

specified "pre-pressures" and three of the five having lower than normal 100-division loads.

Furthermore, the Durometers met with in use do not conform to specifications in the other two respects in which specifications are given, as can be seen from Table II. It is true that the variations in length of pin given in the table are not large, *per se*, but, as the data in Figure 6 show, a slight change in length may make a large change in hardness value, especially at the upper end of the scale. The diameters of base of indentors have been found to vary over a wide range, from 3 per cent below, to 11 per cent above, the specified value. Since the penetration is theoretically inversely proportional to diameter, there would be a wide variation in hardness readings among these five instruments, even when all are set to the same loads.

As a result of the foregoing study of Durometer action, the following procedure for standardization was adopted by the B. F. Goodrich Company, in November, 1936:

1. The instrument is put into good mechanical condition, that is, cleaned, bearings set properly to minimize friction, pointer adjusted, parallax eliminated, and back-lash in the rack and pinion reduced as far as feasible.

2. The base of the pin is examined under a micrometer microscope. If not flat and circular, the pin is either replaced or ground.

3. The load-deflection curve is adjusted to a straight line; the pre-pressure is taken as 57 grams (2 ounces) and the 100 division load as 822 grams (29 ounces) on a 0.0312 ± 0.003-inch diameter indentor. If the diameter of the base is larger, or smaller, than 0.0312 inch, the loads are changed in direct proportion. A tolerance of not more than 5 grams is permitted on the load at any point.

4. The length of pin protruding from the rest plate is adjusted until, when the Durometer is pressed against a flat plate-glass surface, the pointer covers the 100-division mark on the scale.

TABLE II

OBSERVED LENGTHS OF PIN AND BASE DIAMETERS OF INDENTORS OF FIVE TYPE A DUROMETERS

Instrument	Length in.	Deviation from Specification, per cent	Diameter, in.	Deviation from Specification, per cent
Specification	0.09375	.....	0.03125	....
No. 1	0.0951	+ 1.4	0.0347	+ 11
No. 2	0.0933	− 1.5	0.0341	+ 9
No. 3	0.0939	+ 0.2	0.0326	+ 4
No. 4	0.0939	+ 0.2	[a]	....
No. 5	0.1010	+ 7.7	0.0304	− 3

[a] Badly rounded at edge.

5. The final check on adjustments 3 and 4 is made with the back of the case closed tightly by means of both screws.

6. During readings, the Durometer is held with the rest plates F and F' parallel to the surface of the sample, and pressed slowly against the sample with just sufficient force to insure contact. The initial deflection is taken as the reading.

It will be noticed that the departures from manufacturer's standards are few, but that compliance with tolerances is rigorous.

These standards have been in use at the B. F. Goodrich Company for over three years, with approximately 70 Durometers kept under control. Each Durometer is returned regularly for routine inspection at least once a year. If, for any reason, the reliability of a Durometer becomes questionable, it is immediately sent in for adjustment. Thus, over a period of several years, data have been acquired on the performance of the program.

The analysis of the first 20 Durometers which were adjusted is illustrative of the value of this work. It will be noticed (Table III) that the data are divided into two groups. The ten Durometers listed above the dividing rule in the table were standardized according to the procedure given above, those below the rule in the table were calibrated by comparison with standardized Durometers because of the reasons given in the last column. These Durometers could have been standardized if facilities were available for grinding the indentors but this was found unnecessary.

TABLE III

ANALYSIS OF TWENTY REPRESENTATIVE TYPE A DUROMETERS

	Diameter of face, in.	Hardness								Condition of face of indentor
		Sample No. 1		Sample No. 2		Sample No. 3		Sample No. 4		
		Before	After	Before	After	Before	After	Before	After	
No. 1	0.0320	22	22	37	35	74	70	96	96	Flat, small nicks, edge rounded slightly.
No. 2	0.0311	25	23	37	35	72	70	98	96	Flat, edge rounded slightly.
No. 3	0.0271	29	23	39	35	71	70	96	97	Flat, edge rounded slightly.
No. 4	0.0304	28	23	39	35	73	70	100	96	Flat, edge sharp.
No. 5	0.0289	25	22	35	35	64	70	80	96	Flat, edge rounded slightly.
No. 6	0.0303	23	22	36	35	70	70	97	96	Flat, edge sharp.
No. 7	0.0314	23	22	34	35	72	70	100	96	Flat, edge sharp.
No. 8	0.0313	24	22	34	35	70	70	97	96	Flat, edge rounded sharply.
No. 9	0.0305	26	21	37	34	71	70	97	96	Flat, edge sharp.
No. 10	0.0322	24	22	37	34	73	70	101	97	Flat, edge sharp.
No. 11	0.0296	28	22	39	35	73	70	98	96	Out of round, edge rounded.
No. 12	0.0306	27	21	42	34	76	70	99	96	Edge turned over in places.
No. 13	0.0323	28	22	38	35	72	70	98	96	Edge rounded, surface pitted.
No. 14	0.0303	25	22	36	35	70	70	99	96	Edge rounded considerably.
No. 15	.....	31	22	42	35	74	70	95	96	Diameter greater than specification, edge rounded.
No. 16	0.0341	24	23	37	35	74	70	99	96	Diameter greater than specification, edge rounded.
No. 17	0.0349	23	22	33	35	70	70	98	96	Diameter greater than specification, edge rounded.
No. 18	0.0334	25	22	36	35	72	70	98	96	Diameter greater than specification, surface rough.
No. 19	0.0280	25	22	39	35	75	70	98	96	Surface rough and pitted, edge broken.
No. 20	0.0292	18	22	29	34	61	70	84	96	Surface rough, out of round.

The hardnesses given in Table III were obtained by the author. Since the factor of personal prejudice cannot be completely eliminated by any one person, these data do not constitute reliable proof that the standardizing technique is successful. Proof which is independent of the personal factor is presented in Table IV. These data were compiled by Ivan Gazdik, of this laboratory, by collecting readings from six technical men for several compounds tested with their own Durometers—which were standardized by the above method. Only two of the six have had any instruction in the author's technique of reading the Durometer, and only one knew that any comparison was being made.

TABLE IV

PERSONAL VARIATIONS IN STANDARDIZED DUROMETERS

Sample	Hardness read by observer					
	L	Ga	K	F	S	G
A	36	37	36	37 to 38	37 to 38	36
B	33	34 to 35	35	34 to 35	35 to 36	33
C	38	38	39	40	40	37
D	41	41	41	41	41	40
E	55	55	54	53	55	53
F	38 to 39	41	41	..	..	40
G	58	58 to 60	57	..	..	57
H	45	45	45	..	45	45

GENERAL PRINCIPLES OF HARDNESS TESTER DESIGN

Several conclusions can be drawn from this work concerning the design of an ideal hardness tester. Obviously the manufacturer must maintain definite and close tolerances on every variable (including friction) so that his instruments shall be reproducible among themselves. Without such close manufacturing tolerances, the tester will be of little value even if it conforms, in theory, to the correct principles.

The readings given by an ideal tester measure a fundamental physical property of the sample, either the elastic modulus or a related quantity. A portable tester can do this most readily by indicating the force required to produce a specified small indent. The non-portable laboratory instrument can be equipped with several weights and a range of indentor sizes for the measurement of a wide range of hardnesses.

The ideal indentor itself is spherical (ball tipped) rather than cylindrical or "conical". The flat-faced indentor produces infinite compressive stress at the edge of contact (Equation 3), causing abnormal wear at the edge of the indentor, and making the reading sensitive to surface friction. The spherical indentor, on the other hand, receives little wear because the compressive stress drops to zero at the edge of contact. Also, the indentation varies with the cube root of the sphere diameter, rather than with the first power of the cylinder diameter, making the hardness readings with a spherical indentor less sensitive to slight variations from the specified diameter.

The penetration produced by the tester can be any convenient value up to 10 to 15 per cent of the diameter of the spherical indentor. Since existing hardness testers employ a wide range of penetrations, up to 300 per cent of the diameter of indentor, a sample whose true hardness lies at one end of such a scale is being examined at high penetration, but a hardness at the other end of the scale is observed under very low indentation. This is one of the reasons

why the relation between "Durometer hardness" and "shear modulus" is subject to so much controversy in discussions about rubber mountings.

The sample whose hardness is being measured must be thick enough to eliminate the effect of the supporting surface, the minimum thickness being about $10\sqrt{dD/2}$. With testers now available it is possible to reverse the order of hardness of two samples as given by different Durometers if the softer sample is considerably thinner than the other.

The ideal hardness tester has within itself means for establishing a reference plane of penetration. In the dead-weight instrument the zero plane can be approximated very closely by the application of a load which is negligible compared to the load under which the penetration is measured. Since the suggested portable tester measures force at a fixed penetration, the reference plane is determined by a flat annular plate on the bottom of the case, around the indentor. This plate must not in any sense be a "pressure foot". Pressure applied to the rubber over an annular ring forces the rubber up into the hole, producing a false reference plane. In addition, rubber under compression is harder than normal. Consequently, the portable Durometer is pressed against the sample with just sufficient force to insure contact between sample surface and reference plane.

It should be realized that the ideal hardness tester considered here will give reproducible readings on a perfectly elastic material. However, if the sample shows any elastic after-effect, such as is present in rubber, the actual hardness will depend on the rate of application of load, just as it depends on the temperature and degree of stretch of the sample. All of these factors must be fixed to attain agreement on even empirical "hardness" measurements throughout the industry.

REFERENCES

[1] 1939 Book of A. S. T. M. Standards, Part III, p. 347.
[2] 1939 Book of A. S. T. M. Standards, Part III, p. 855.
[3] Larrick, "The hardness of rubber and other highly elastic materials", *Phys. Rev.* **57**, 358 (1940).
[4] Symposium on rubber, Cleveland Regional Meeting, Am. Soc. Testing Materials, 1932, p. 96.

THE APPLICATION OF LATEX TO HIGHWAY AND FLOOR SURFACING *

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INTRODUCTION

Investigations on the development of latex mixtures for roadways were carried out in Malaya by Hastings during the period 1931 to 1933[1]. Of the different mixtures tried, those containing aluminous cement gave the most promising results. Considerable progress of a practical character in working out the details of a suitable cement-latex mixture was then made, culminating in the laying in 1933 of an experimental section of road 4.5 miles from Kuala Lumpur on the Kuala Lumpur—Port Swettenham Road, where the traffic is fast and fairly heavy. In view of the promising results obtained in these experiments, it was agreed that the subject should be studied further in London, and that particular attention should be given to obtaining a better understanding of the fundamental principles involved in the preparation of latex mixtures for road and floor surfacing. As the economic factors are less exacting for flooring than for highways, it was decided that the application of latex mixtures to flooring should receive prior attention. The main purpose of the investigation has now been fulfilled, and this paper presents a summary of the work carried out and the results obtained.

Mixtures of aluminous cement and latex have been in use for some time, both for flooring and other purposes; as early as 1923-4 patents were obtained for mixing cement with specially treated latex. The theory underlying this process is that the cement combines with the water of the latex and becomes hydrated, the latex losing its water and coagulating. How far this occurs in practice was not established at the outset of the work in London, and attempts were made to determine the extent of hydration of the cement and to examine the microstructure of the mixtures. During the course of this work it became apparent that the structure and physical characteristics of the products were largely dependent on the materials used in compounding and especially on the latex stabilizer. A systematic study of the principles underlying the compounding of the mixtures was then undertaken, and the relationship between compounding and physical properties determined. It thus became necessary to develop a series of tests to measure the physical properties, as no suitable methods were available. As a result of these experiments, a number of cement-latex compositions were developed and the most suitable selected for small scale trials. A summary of the work carried out and the conclusions reached are given in the following sections.

(1) MICROSCOPIC INVESTIGATION

In the microscopic examination of cement-latex mixtures, a study was made of the changes occurring when cement is mixed with latex; also, the product obtained after setting was examined.

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In following the changes which occur when cement is mixed with latex, it was found necessary to employ a very dilute latex (about 2 per cent dry-rubber content) and to use finely ground cement to obtain layers sufficiently thin to permit of examination by transmitted light. When cement is mixed with water, hydration of the cement occurs, and various crystalline products of hydration and deposits of amorphous material are formed; these may be recognized by their crystal habit and by staining reactions. When dilute latex was added to cement, the crystal growth was found to be strongly inhibited, but no conclusions could be drawn regarding the formation of amorphous deposits, owing to the presence of latex particles making observation difficult; however, staining reactions indicated the presence of some hydration products. On the other hand, in the presence of latex containing alkalies, *e.g.*, caustic potash, crystal growth was greatly increased, the period required for crystal formation being much less than in the case of cement and water alone. Other materials, chiefly stabilizers of latex such as saponin, showed the reverse effect, crystal growth being greatly retarded.

In the examination of set cement-latex mixtures, the usual methods of hand-sectioning by cutting or grinding were found to be unsuitable, owing to the nature of the material; a heavy sledge microtome was useless, as the hard cement grains spoiled the razor edge, and grinding the material under liquid air was only partially successful owing to curving of the specimen as it thawed out. The method eventually used was to vulcanize the material by immersing it in molten sulfur (at 135° C for about 20 hours) and then to grind the surface according to the practice employed in preparing rock sections. This method is open to the objection that a modification of the rubber phase must occur; the distribution of the mineral components, however, will probably not be changed.

The appearance of sections, both by reflected and transmitted light, indicated the presence of incompletely hydrated cement grains embedded in a matrix of cement hydration products and rubber. With an increasing proportion of rubber the proportion of matrix increased. Mixtures containing alkaline materials, which were found to accelerate crystal growth, showed a more highly crystalline appearance and also clusters of amorphous material deposited at intervals in the matrix. Through the medium of staining reactions and an examination through crossed nicols, these clusters were shown to be aluminum hydroxide. Both with materials accelerating crystal growth and those retarding it, a fine grained structure was observed in the matrix, which was thought to be caused by the deposition of colloidal aluminum hydroxide on the latex particles during coagulation.

(2) HYDRATION OF CEMENT IN ALUMINOUS CEMENT-LATEX MIXTURES

The mircroscopic examination of mixtures of cement and latex showed that the extent of the chemical reaction between aluminous cement and water is changed by the presence of latex and certain other materials. Experiments were carried out therefore to determine the effect of these materials on the combination of cement with water.

Specimens containing known proportions of cement, latex and the required material (chiefly latex-stabilizing agents) were prepared in small dishes and stored in a closed vessel at constant temperature. Determination of the combined water was made at intervals by removing a specimen, weighing and drying overnight to constant weight, care being taken to prevent oxidation of the rubber. Experiments were made with varying proportions of cement to rubber

in the presence of such materials as saponin, casein, caustic potash and serum solids. It was found that the quantity of water chemically combined and that mechanically held depended on the type of stabilizer added. After keeping for one month, caustic potash mixtures contained 11 per cent of combined water, in addition to 10.7 per cent of water which could be driven off by heating at 105° C, whereas in a similar mixture containing saponin only 1.5 per cent of water was combined and 4 per cent mechanically held. The serum substances in latex were found to decrease the rate of combination of cement and water, but they did not appear to reduce the amount of water finally combined.

(3) PRINCIPLES OF COMPOUNDING

It was apparent, as a result of the work on microstructure and the hydration experiments, that considerable differences might be anticipated in the properties of cement-latex mixtures prepared with various stabilizers, and a systematic examination of the modifications produced by various stabilizers was undertaken. As a result of these experiments, it was found that whereas the majority of stabilizers such as casein and saponin retarded the setting of the cement, a few materials such as caustic potash, gum arabic and triethanolamine accelerated it. The cement-latex compositions produced by these two types of stabilizer, respectively, were: (1) a soft rubbery material containing a small proportion of combined water, and (2) a hard, cementitious product, containing a high proportion of combined water. The type of product obtained could thus be controlled by the stabilizer used in preparation.

For practical purposes it is necessary that cement-latex mixtures should remain in a stable or "workable" condition for one-half to one hour, and that they should set hard within two or three days. Two tests were devised therefore to measure these properties, *viz.*, a stability test, which consisted in determining the period during which the mixture could be kept without coagulating when rubbed in a pestle and mortar for 15 seconds, and a setting test, which consisted in observing the period which elapsed before attaining a certain arbitrary degree of hardness, measured by the indentation of a standard loaded needle.

By the aid of these tests it was a simple matter to evaluate the stabilizing capacity of a number of substances and to control both the setting time and the hardness of the final product by adjusting the proportion of materials retarding and accelerating the cement set. The soft rubbery product obtained by reducing the proportion of the material accelerating the setting of the cement showed a tendency to crack, owing to shrinkage caused by evaporation of water. This phenomenon had previously been observed by Hastings[1] and had been successfully overcome by incorporating sodium silicofluoride as a delayed coagulant; this material, however, has an acid reaction and so inhibits the hydration of the cement, resulting in a long drying period, especially under conditions of a temperate climate. Attempts were made therefore to discover a delayed coagulant which had an alkaline reaction. A combination of calcium cyanamide and sodium metasilicate was found to be satisfactory for this purpose, the coagulation depending on a slow removal of the stabilizing agent (sodium metasilicate) and a subsequent liberation of calcium ions, which also accelerate the setting of the cement.

The relation between the time of the coagulation of the latex and the setting of the cement was found to be important in controlling the type of product obtained. If the latex remains stable during the setting of the cement the rubber particles tend to become surrounded by cement hydration products and do not

readily form a continuous phase. On the other hand if the latex coagulates before the cement sets, there is a tendency for the cement particles to become coated with rubber, and this inhibits further hydration and setting. It is not particularly difficult, however, to obtain conditions in which the rubber coagulates during the hydration and setting of the cement, so that an intimate mixture of cement hydration products and rubber is obtained.

When laying cement-latex compositions, it is necessary to control the viscosity of the mixtures, in some instances a thin cream being desirable and in others a stiffish paste. The addition of wood-flour or inert fillers was found to thicken the mixtures considerably; flocculation of the latex, by calcium chloride for instance, proved also to be a useful method. To reduce the viscosity, sodium silicate, caustic potash and most wetting agents, such as saponin and Igepon T, were found very efficient. The action of these substances probably does not depend as much on changes in the viscosity of the latex as on changes in the cement-water suspension.

The production of brightly colored aluminous cement-latex mixtures is not an easy matter, owing to the dark grey color of the cement, but by using a white filler and brightly tinted pigments pleasing colors can be obtained. Care has to be used in selecting the colors, as many of them react with strong alkalies such as lime and caustic potash; satisfactory results have been obtained with "Fast-lime" colors.

Despite taking all reasonable precautions to standardize the ingredients and the conditions of mixing cement-latex compositions, variation in stability, setting-time, viscosity and properties of the final product sometimes occurs. This was found to be due to variations in both the cement and the latex, neither of which can be reproduced exactly from batch to batch. These variations are a hindrance to the commercial development of the products, and experiments are being carried out to determine the causes. The results obtained with many stabilizing agents indicate that the resistance of latex to mechanical coagulation falls off considerably on storage, especially in the presence of strong alkalies; in one instance the stability was reduced to one-fifth of its value after keeping for three days.

Nearly all cement-latex mixtures contain aggregates added either for cheapness, decorative purposes or to modify their properties. Most of the materials used as aggregates in cement and terrazo work have proved to be suitable for this purpose. Such materials as granulated cork, shredded waste rubber, wood chips, and asbestos fibre may be added to give pleasing decorative effects and to lower the cost, but care must be taken to ensure that the aggregate is clean and that it is unlikely to react chemically with other components in the mixture. Experiments also showed that it is necessary that the aggregate should be graded with regard to particle size in such a manner as to give a fair proportion of each size of particles ranging from the largest added to that of the coarsest cement grains. It was found that grading not only increased the strength of mixtures and reduced the proportion of binder required for a given aggregate, but also assisted greatly in giving mixtures which were easily trowelled.

Experiments have been made replacing aluminous cement with Portland cement, attention being given chiefly to the white variety known as Snowcrete. The products obtained by mixing Snowcrete and latex did not possess such good physical characteristics as those obtained with aluminous cement; either they showed excessive shrinkage or they were hard, and often tended to be friable with a rather low tensile strength. The difference in the nature of the

products formed from Portland and aluminous cements is probably due to the different hydration processes involved in the two processes. With aluminous cement it has been shown that colloidal aluminum hydroxide is produced, whereas with Portland cement crystalline calcium hydroxide is formed, and it is obvious that a more intimate dispersion would be obtained with colloidal aluminum hydroxide in latex than with crystalline calcium hydroxide. Experiments are being made to prevent the formation of lime crystals in the hope of improving the cement-latex product obtained. An alternative is to provide a third substance which will give a good bond between lime and latex particles.

(4) METHODS OF MIXING

The thicker mixtures, especially those containing aggregate, are conveniently mixed in a Werner-Pfleiderer machine. With mixtures of the consistency of thin cream, a simple inverted T-shaped stirrer revolving at a speed sufficient to give a good vortex has been found satisfactory. It is of course necessary to add the stabilizer first when compounding the latex, otherwise flocculation or coagulation of the latex may follow. Generally it has been found convenient to mix the stabilizing and vulcanizing ingredients with the latex and the dry materials such as pigments and fillers with the cement. Care must be taken in selecting stabilizers and accelerators of the cement set so that interaction between them does not occur.

(5) RELATION OF THE COMPOSITION OF MIXTURES TO PHYSICAL CHARACTERISTICS

It has been stated already that latex stabilizers and accelerators of the cement set exert a profound effect on the properties of cement-latex mixtures. Marked differences are also brought about by varying the proportion of cement to rubber, varying the proportion of water and incorporating various filling materials. A brief account is given of the effect on the physical characteristics of the mixtures of (a) the rubber:cement ratio, (b) the water:cement ratio, (c) vulcanizing ingredients, and (d) various fillers and aggregates.

(a) Effect of Various Proportions of Cement and Rubber

Experiments have shown that with a higher proportion of cement to rubber than 100:20, a hard cementitious product is formed, with little advantage over cement alone. The tensile strength of the mixtures was found to increase with increasing proportions of rubber, and the resistance to compression to decrease. The coefficient of restitution, a measure of the elasticity, increased with increasing proportions of rubber.

(b) Effect of Varying the Proportion of Water

Specimens prepared with proportions of water increasing from 15 per cent to 35 per cent (reckoned on the cement) showed a progressive decrease in tensile strength. The observed values for resistance to compression were inclined to be irregular, but there appeared to be an optimum proportion of water for each mixture. Determinations of the linear contraction on setting showed that increased proportions of water did not necessarily result in greater shrinkage; the greatest shrinkage was in some cases found in mixtures containing the lowest

proportions of water. Thus a mixture containing 15 per cent of water showed a linear contraction of 4.4 per cent, whereas the same mixture with 25 per cent water showed only 1.8 per cent.

(c) Effect of Adding Vulcanizing Ingredients

Experiments undertaken to determine the effect of vulcanizing ingredients showed that these had little effect on the mechanical properties of freshly prepared cement-latex mixtures. Accelerated aging tests and natural aging tests over a period of twelve months suggested, however, that with certain mixtures vulcanizing ingredients gave better aging properties.

(d) Effect of Fillers and Aggregates

It was found that 35 per cent of the cement in mixtures containing 100 parts of cement to 30 parts rubber could be replaced by inert fillers, such as limestone dust, without appreciably altering the resistance to compression. The replacement of this quantity of cement did not alter appreciably the tensile and compressive strengths of the softer mixtures, but reductions in the strengths of the harder types were observed.

Ungraded aggregates such as marble chippings generally reduced the tensile strength of the product; softer aggregates such as granulated cork produced a marked decrease in tensile and compressive strengths. The coefficient of restitution also was greatly influenced by the type of aggregate used; granulated cork and shredded waste rubber gave products of high elasticity, whereas marble and granite chippings had the opposite effect. The most satisfactory products generally were obtained when the physical characteristics of binder and aggregate were similar.

(6) PHYSICAL TESTS

Having prepared a number of cement-latex compositions, it was necessary to devise means whereby their physical characteristics could be compared. A series of physical tests were developed therefore which comprised the measurement of (a) tensile strength, (b) compressive strength, (c) hardness by indentation and recovery, (d) coefficient of restitution, (e) water absorption, (f) aging, and (g) contraction during setting. Further tests still being developed include the measurement of the resistance to impact-abrasion, adhesion, coefficient of friction, electrical and thermal conductivities, acoustic properties, fire resistance, ease of cleansing and effects of oils, fats, waxes and detergents. The development of these tests has necessitated devising in most cases a new test procedure; in the case of the compressive strength, tensile strength and coefficient of restitution tests new machines specially adapted for the purpose have been designed and constructed. All specimens were aged for at least one month before testing.

(a) Tensile Strength

Tensile test determinations are carried out on a machine built in the laboratory workshops. The machine is of the simple-lever type, resembling the Adie cement-tester; it is fitted with special grips and an electrically controlled device which enables the stretch of the specimen to be taken up.

Difficulty was experienced with tensile strength determinations, owing to irregularities in the breaking load values. This has been overcome largely by

adopting a carefully standardized method of preparation of the specimens and by using specially shaped test-pieces. For hard mixtures the test-piece is moulded in the form of a briquette, as specified by the Argentine Government for cement testing; for soft rubbery mixtures a flat dumbbell piece held between wedge-action grips is used. Values for the breaking load can now be reproduced generally within limits of 15 per cent, provided an average of at least 6 test-pieces is taken for each determination.

As an alternative to the direct determination of tensile strength, transverse breaking tests have been attempted. Although they have the advantage of requiring neither special grips nor elaborate shaped test-pieces, it was found that the rubbery specimens could not be broken by this means, as they easily bent and pulled through the supports. Transverse testing therefore has been discontinued.

(b) Compression Tests

A machine suitable for compression testing also has been built in the workshops. This machine has the advantage that an autographic record is obtained showing the stress-strain relationship when a small cylindrical specimen 2 inches in diameter and 1.5 inches in height is subjected to compression. It has been shown that two distinct types of stress-strain curve can be obtained with cement-latex mixtures, one resembling that of cement, the other resembling highly compounded rubber. A third type combining both these characteristics is thought to represent one of the most satisfactory types of mixture. The results obtained are readily reproducible.

(c) Hardness

To determine the resistance to indentation, the specimens are supported in a surrounding ring of concrete and the middle of the specimen is subjected to a load of 1,000 pounds per square inch for one minute, the load being transmitted to the specimen by means of a circular plunger. The indentation under load and the permanent deformation are recorded.

(d) Coefficient of Restitution

It was found that the apparatus commonly used for measuring the coefficient of restitution (the sclerometer) was unsuitable for many cement-latex compositions, owing to the non-homogeneous nature of the material. Satisfactory tests were carried out, however, by using a large pendulum, the bob of which consists of a steel sphere 2.25 inches in diameter; this is allowed to fall from a standard position and to rebound from the surface of the specimen. The height of rebound is estimated from the time required for the bob to come to rest against the specimen, an electrical device indicating this position.

(e) Water Absorption

Water absorption is measured as the percentage increase in weight of a cleaned specimen suspended in distilled water for a given time at room temperature.

(f) Aging

Two types of aging test are carried out: (1) accelerated aging, by storing the specimens for a number of days at 100° C; (2) natural aging by storing

specimens for a period of twelve months, some being exposed to outside atmospheric conditions, others being stored indoors. Measurements are made of the changes in tensile and compressive strengths.

(g) Contraction

An apparatus has been constructed for measuring volume shrinkage of cement-latex specimens during setting and hardening. Some determinations have been made with this apparatus, but the majority of the results obtained were direct measurements of linear contraction taken on tensile test-pieces.

(7) COMPARISON OF CEMENT-LATEX MIXTURES WITH OTHER FLOORING MATERIALS

A number of cement-latex compositions now commercially available for flooring have to compete with established flooring materials, and it was considered that it would be of interest to compare the properties of these materials, prepared either commercially or in the London Advisory Committee laboratories, with other types of flooring materials such as mastic asphalt, concrete, magnesite, deal and oak. All the materials tested were subjected to compression, tensile, indentation, coefficient of restitution and water-absorption tests, using identical conditions as far as possible.

It was found that the compressive strength of cement-latex mixtures varied over a fairly wide range, certain of the mixtures being more easily crushed than deal, others being more difficult to crush than oak, but none had the compressive strength of concrete or magnesite.

Tensile strength determinations showed that cement-latex mixtures have a strength similar to mastic asphalt, rather less than that of magnesite or concrete material, and much less than that of wood. Indentation tests indicated an exceptionally wide "hardness" range—the results showing values varying from those of hard magnesite flooring to those of materials softer than any of the nonrubber compounds examined. Recovery after indentation showed that cement-latex mixtures are similar to wood, asphalt and magnesite. Measurements of the coefficient of restitution demonstrated the rubbery nature of cement-latex compositions, some of the materials showing a resiliency greater than that of any of the other materials tested. Water absorption experiments indicated that cement-latex mixtures do not absorb so much water as some of the other materials examined, for example, wood; on the other hand they are not as resistant to water as mastic asphalt, which is of course highly impervious. Magnesite absorbed considerably more water than the majority of the cement-latex mixtures, which in some cases were superior even to concrete.

The results of these comparative tests showed that commercial cement-latex mixtures possess physical properties similar to those of other flooring materials, but they have the important advantage that their resilience can be increased to a value exceeding that of any other nonrubber flooring material. The range in properties of the mixtures is very wide, and by making small adjustments in composition it is possible to obtain material nearly as hard as cement or softer than asphalt. The mixtures possess many valuable properties not indicated by these experiments; they appear to give an excellent non-skid surface, which when wet is retained to a high degree. They have good heat-insulating and sound-deadening properties, they are resistant to oil and chemicals and, unlike magnesite, they do not corrode metals.

(8) PRACTICAL TRIALS

Although laboratory tests give a useful indication of the relative merits of a series of mixtures as flooring materials, it is obvious that the only reliable method of estimating the value of a given mixture is by means of a service test. A number of trials have been carried out therefore by laying the mixtures under conditions where heavy traffic is encountered, observations being made on (1) the ease and suitability of laying, and (2) the finished appearance and wearing properties.

Two series of mixtures were laid, one incorporating a fairly hard binder, the other a soft rubbery binder; in all cases aggregate such as marble chippings, granite chippings, sand, asbestos, cork, and shredded waste rubber was added. A Werner-Pfleiderer mixer was employed for the preparation of most of the mixings, patches of about 20 to 25 pounds of material being mixed and laid by trowelling, the most efficient method found being to lay the mixture a little at a time and not to spread a whole batch over the floor surface at once. Some of the mixtures were finished by hand, the surface being trowelled smooth as when laying concrete; others were allowed to harden and the surface then buffed with a sanding machine, exposing aggregate in section and thus introducing a terrazo effect.

The following trials have been made:

(1) Three flights of stone steps receiving a fair amount of traffic were refaced with the hard cement-latex mixture containing granite, marble and shredded waste rubber as aggregate, respectively. Each flight of steps is wearing satisfactorily, one having been laid for two years, the others for about eighteen months.

(2) Various floor surfaces, some of wood and some of stone, have been covered with different mixtures; both the rubbery and hard types of mixtures appear to be satisfactory after a year's wear. A surface exposed to all weather conditions was divided into two portions. One portion was covered with a material containing vulcanizing ingredients, the other with the same material without vulcanizing ingredients; after six months both surfaces appear to be equally satisfactory, with no apparent differences.

(3) A section of the laboratory floor was laid with a rubbery mixture containing shredded waste rubber. This was not successful, owing to poor adhesion at the joints where one batch was finished and the next one started.

(4) A piggery at the Hertfordshire Farm Institute, St. Albans, was laid in two sections with a hard mixture, one containing granite chippings, the other shredded waste rubber. The piggery was laid about twelve months ago and is satisfactory except for a portion where the pigs have rooted out some of the waste rubber aggregate.

(9) APPLICATIONS

The potentialities of these cement-latex mixtures are now becoming more generally recognized commercially. Not only are they being used as flooring materials in public buildings, offices and workshops and in shipbuilding, but they are also being utilized for water-proofing walls, as linings for tanks which have to hold corrosive liquids, as pipe-jointing material, for surfacing tennis courts and in the construction of pedestrian crossings. Other possibilities include their use for cementing glass to other materials, as an adhesive for mounting tiles, and as a resilient covering for rollers used in the spinning of flax and similar

materials. These applications have been discussed with the appropriate commercial organizations.

A paper read before the Institution of the Rubber Industry[2] gave in greater detail the results of the work outlined in this paper, and a patent[3] was obtained in May 1937 protecting certain methods of compounding these materials.

During the course of the work a considerable number of enquiries regarding cement-latex mixtures have been dealt with, and advice has been given on the procedure of preparing and laying the mixtures. Contact has been maintained with commercial firms interested in these materials, with the Building Research Station, Watford, and with the Highways Department, Imperial College of Science and Technology, from whom many helpful suggestions have been received during the course of the work.

Thanks are due to the London Advisory Committee for Rubber Research (Ceylon and Malaya) for permission to publish this paper, to G. Martin and to W. S. Davey for helpful suggestions and criticisms, and to A. T. Faircloth and R. Stacey for assistance in carrying out the practical work.

REFERENCES

[1] Rubber Research Inst., *Annual Report* **1932**, 114; **1933**, 136.
[2] *Trans. Inst. Rubber Ind.* **13**, 189 (1937).
[3] British patent 484,712.

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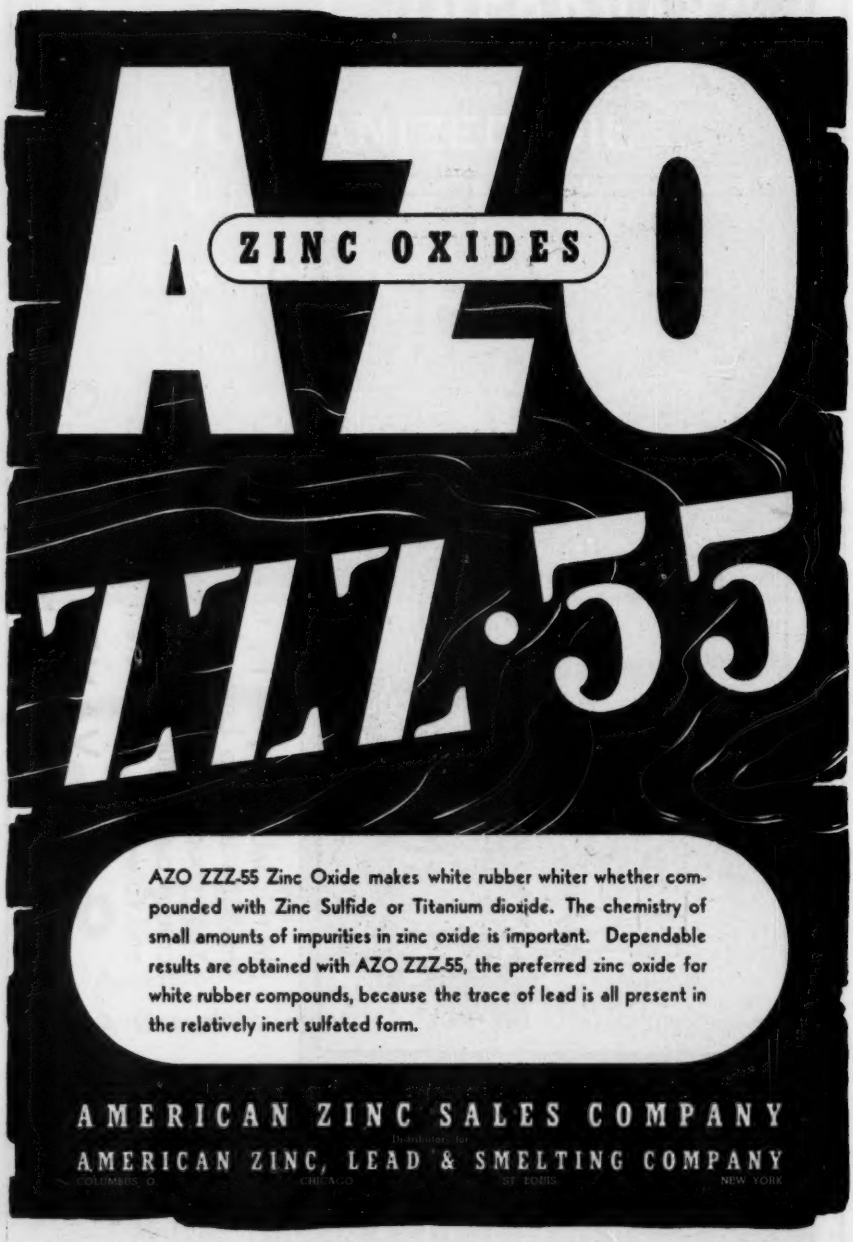
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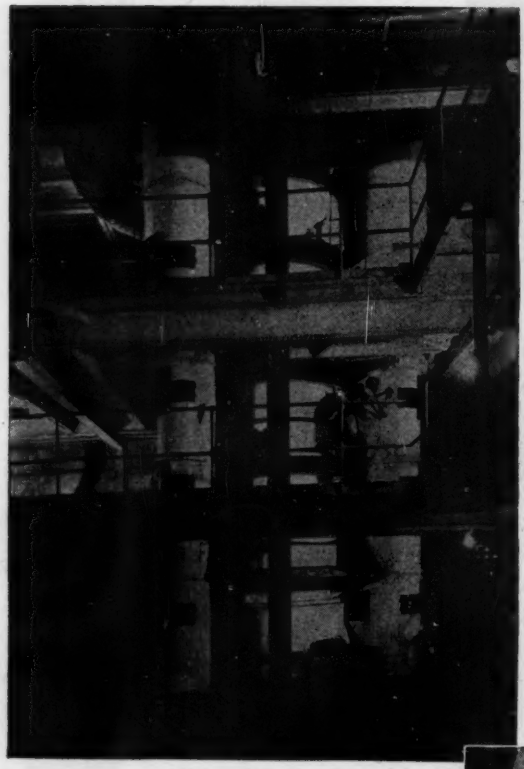

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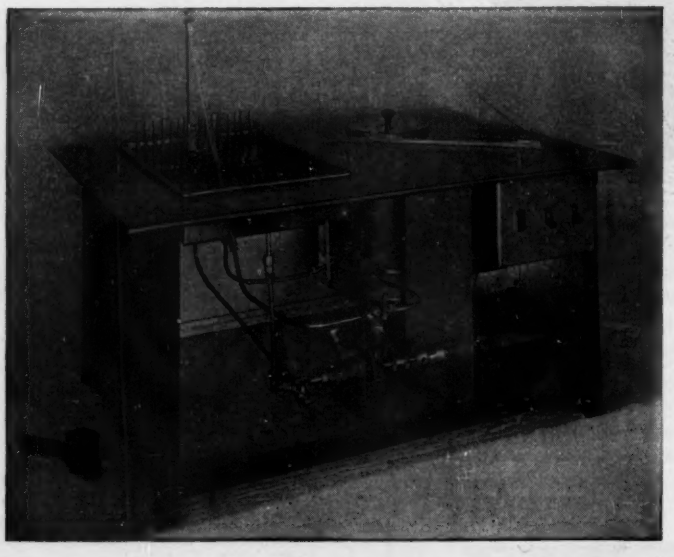

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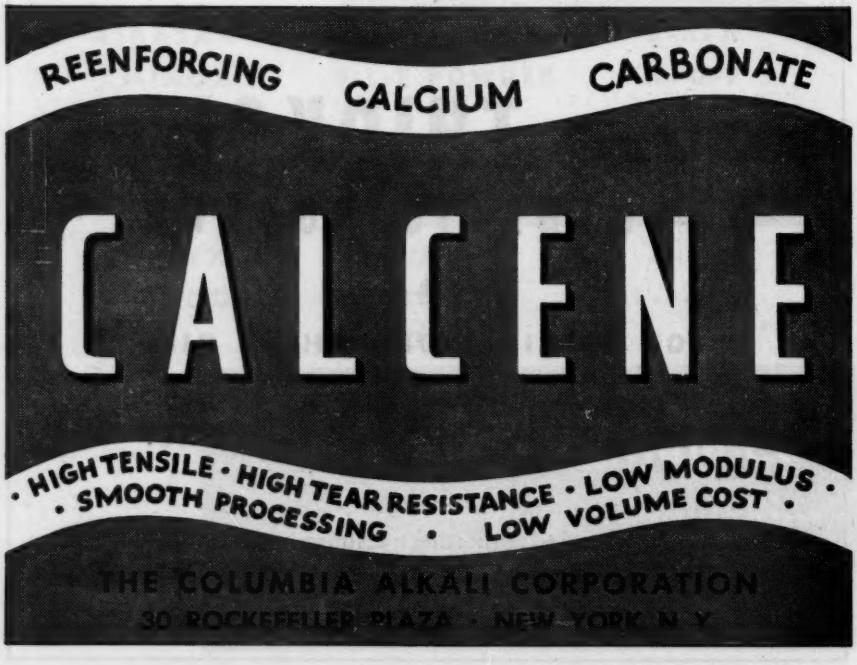
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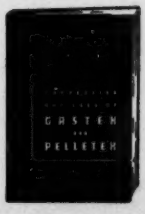

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